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Space-Temperature Correlations in Quantum Statistical Mechanics

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ABSTRACT

In this work some approaches used in classical statistical mechanics for deriving integral equations for the pair distribution function have been generalized to quantum systems. In the functional differentiation method, distributions depending on space and temperature arguments are generated from the grand partition function in external field. These distributions are diagonal elements of Green's functions and represent physical quantities when temperature arguments are set equal. A given distribution can be expanded in the external field by means of a functional Taylor series. An integral equation results when the external field is specialized to one arising from a number of fixed particles via their pair interaction with the remaining particles. In this case a distribution in external field may be converted to a higher order distribution for a uniform system. This process is accomplished by using a Feynman path integral representation for all quantities. Classical and quantum statistics are treated. In the former case the problem of bounds on distributions is also investigated. An alternate approach, the potential ensemble method, applies to Debye-Hückel sequences. Here one, e.g., replaces

the actual density (with a particle fixed) by one in which a pair interaction of particles is replaced by an external field, but an ensemble average must be taken over all external fields. A steepest descent calculation enables one to find the pair distribution and best external field self-consistently. The quantum formulation of this method requires all quantities to be expressed on a lattice in occupation representation, in which a lattice site is specified by position in space, temperature and particle number. Agreement between the two methods described here is indicated.

1. Introduction

Techniques exist for deriving integral equations for the pair distribution in classical statistical mechanics [1]. In one of these, one first functionally differentiates the grand partition function with respect to an external potential generating coordinate distributions. Then one performs a functional Taylor expansion between two quantities dependent on the external potential, as density v. potential. One completes the derivation by using a relation which connects lower to higher distributions. This relation involves "fixing" one or more particles. In this fashion integral equations of the Debye-Hückel [2], Percus-Yevick [3], Kirkwood-Salsburg [4] and Mayer-Montroll [5] types can be derived. In addition, rigorous bounds on distributions are obtainable by truncating the latter two sequences, retaining the remainder [1], [6].

Another technique [7], at least for Debye-Hückel sequences, permits us to replace the actual density (tied to a fixed particle) by one in which the internal potential is replaced by an external one and an ensemble average is taken over all external potentials. A steepest descent calculation enables one to find the pair distribution and "best" external potential self-consistently.

This work generalizes the above to quantum systems. After a brief survey of classical theory, we begin in Section 3 by introducing the distributions appropriate to quantum

systems. These functions have space and temperature arguments but are less general than Green's functions, being only diagonal elements of them. The observable distributions are found by setting temperature arguments equal. An integral representation of the grand partition function is crucial to the generalization of the Taylor series method, and is carried out via the Feynman path integral [8] in Section 4. In later sections we see to what extent the tools developed can provide us with integral equations and bounds for the pair distribution. The "potential ensemble" [7], [9] method and its generalization is discussed in the last three sections.

2. Survey of Classical Theory

The canonical partition function for a classical N particle system is

$$(2.1) \qquad Z_N = \int dx_1 \, .. \, dx_N \, dp_1 \, .. \, dp_N \exp - \beta H_N ,$$

with

$$(2.2) \qquad H_N = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j} \phi(x_i, x_j)$$

and $\beta = (kT)^{-1}$. The grand partition function is a weighted average

(2.3) $$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{N!} \quad Z_N$$

which upon doing the momentum integrations becomes

(2.4) $$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int dx_1 \,..\, dx_N \quad \exp - \beta \sum_{i<j} \phi(x_i, x_j)$$

with

$$z = e^{\beta\mu} \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2} .$$

The sth particle distribution is defined as

(2.5) $$n_s(x_1' \,..\, x_s') =$$

$$\mathcal{Z}^{-1} \sum_{N=s} \frac{z^N}{(N-s)!} \int dx_1 .. dx_N \quad \exp - \beta \sum_{i<j} \phi(x_i, x_j)$$

$$\cdot \; \delta(x_1 - x_1') \,..\, \delta(x_s - x_s') \; ,$$

and is gotten from $\mathcal{Z}$ by appending an external potential $\sum_{i=1}^{N} U(x_i)$ to it and taking functional derivatives. In general,

(2.6) $$\frac{\delta^s \mathcal{Z}[U]}{\delta e^{-\beta U(x_1)} \ldots \delta e^{-\beta U(x_s)}} = \mathcal{Z}[U] e^{\beta U(x_1)} \ldots e^{\beta U(x_s)} n_s(x_1 .. x_s | U) \; .$$

Modified distribution, whose arguments can refer to identical particles are given by

(2.7) $$\hat{n}_s(x_1 \,..\, x_s | U) \mathcal{Z}[U] = \frac{\delta^s \mathcal{Z}[U]}{\delta\text{-}\beta U(x_1) \ldots \delta\text{-}\beta U(x_s)} \; , \text{ e.g.,}$$

$$(2.8)\quad \hat{n}(x) = n(x),\ \hat{n}_2(x_1x_2) = n_2(x_1x_2) + n(x_1)\delta(x_1 - x_2)\ ,$$

$$\hat{n}_3(x_1x_2x_3) = n_3(x_1x_2x_3) + n_2(x_1x_2)\delta(x_2 - x_3)$$

$$+ n_2(x_2x_3)\delta(x_3 - x_1) + n_2(x_3x_1)\delta(x_1 - x_2)$$

$$+ n(x_1)\delta(x_2 - x_3)\delta(x_3 - x_1), \ldots\ .$$

Ursell functions, which vanish whenever one particle is uncorrelated with the others, are given by

$$(2.9)\quad F_s(x_1 \,..\, x_s|U)\ e^{\beta U(x_1)} \ldots e^{\beta U(x_s)}$$

$$= \frac{\delta^s \log \mathfrak{Z}[U]}{\delta e^{-\beta U(x_1)} \ldots \delta e^{-\beta U(x_s)}}\ ,\ \text{e.g.,}$$

$$(2.10)\quad F(x) = n(x),\ F(x_1x_2) = n_2(x_1x_2) - n(x_1)n(x_2)\ ,$$

$$F(x_1x_2x_3) = n_3(x_1x_2x_3) - n(x_1)n_2(x_2x_3) - n(x_2)n_2(x_1x_3)$$

$$- n(x_3)n_2(x_1x_2) + 2n(x_1)n(x_2)n(x_3), \ldots\ .$$

Finally, modified Ursell functions:

$$(2.11)\quad \hat{F}_s(x_1 \,..\, x_s|U) = \frac{\delta^s \log \mathfrak{Z}[U]}{\delta{-}\beta U(x_1) \ldots \delta{-}\beta U(x_s)}\ ,\ \text{e.g.,}$$

$$(2.12)\quad \hat{F}_1 = \hat{n}_1,\ \hat{F}_2 = \hat{n}_2 - \hat{n}_1\hat{n}_1,\ \hat{F}_3 = \hat{n}_3 - \sum \hat{n}_2\hat{n}_1 + 2\hat{n}_1\hat{n}_1\hat{n}_1, \ldots\ ,$$

as in (2.10).

Consider now a t-particle distribution with s other particles $x_1 \ldots x_s$ held fixed. The fixed particles provide an external field to the remaining ones because of the pair interaction. Explicitly,

$$(2.13) \qquad U_\phi(y) = \sum_{j=1}^{s} \phi(y, x_j) \ .$$

It can be shown that

$$(2.14) \quad n_t(y_1 \ldots y_t | U_\phi) = \frac{n_{s+t}(x_1 \ldots x_s, y_1 \ldots y_t)}{n_s(x_1 \ldots x_s)}$$

and

$$(2.15) \quad \mathfrak{z}[U_\phi] = z^{-s} \, n_s(x_1 \ldots x_s) \mathfrak{z} \cdot \exp \beta \sum_{i<j<s} \phi(x_i x_j) \ . \ ^*$$

As a simple application of (2.11), (2.8) and (2.14), the latter with s = t = 1, expand $n_1(y|U_\phi)$ in a functional Taylor series against U_ϕ.

With $U_\phi(y)$ now just $\phi(y,x)$,

$$(2.16) \quad n_1(y|U_\phi) = \frac{n_2(yx)}{n(x)} = n(y) + \int \frac{\delta n(y)}{\delta \beta U_\phi(z)} \Big|_{U=0} \beta\phi(z - x)dz + \ldots ,$$

$$(2.17) \quad \frac{n_2(yx)}{n} = n - \beta \int dz(n_2(yz) + n\delta(y - z) - n^2)\phi(z - x) \ .$$

This is the Debye-Hückel equation [2], solvable by Fourier transformation. While (2.17) is valid for weak potentials,

* Note: (2.14) follows from (2.15) by applying (2.6).

other choices for functionals in the Taylor series are indicated if the potentials should be singular. For example $ne^{\beta U}$ v. $e^{-\beta U}$ to first order yields the beginning of a Kirkwood-Salsburg type hierarchy.

We next consider a way of finding bounds on distributions [1].

For non-negative potentials, $\omega(x) = e^{-\beta U_\phi(x)} - 1$, (the Mayer-f function), is ≤ 0, and

$$(2.18) \qquad \int n_s(x_1 \,..\, x_s)\omega(x_1) \,..\, \omega(x_s) dx_1 \,..\, dx_s$$

has the sign of $(-1)^s$, as distributions are non-negative. Taking advantage of this fact we expand

$$n_t(y_1 \,\ldots\, y_t | U_\phi)\mathfrak{z}[U_\phi] \exp \beta \sum_{i=1}^{t} U_\phi(y_i)$$

against $e^{-\beta U_\phi}$. Here we choose $U_\phi(y) = \sum_{j=1}^{s} \phi(y, x_j)$. With the help of (2.6), (2.14) and (2.15) the full expansion with remainder is:

$$(2.19) \quad n_{s+t}(x_1 \,..\, x_s, y_1 \,\ldots y_t) z^{-s} \exp \beta[\sum \phi(x_j y_i) + \tfrac{1}{2} \sum{}' \phi(x_i x_j)$$

$$= \sum_{m=0}^{\ell} \frac{1}{m!} \int dz_1 \,\ldots\, dz_m \, \omega(z_1) \,\ldots\, \omega(z_m)$$

$$n_{t+m}(y_1 \,\ldots\, y_t, z_1 \,\ldots\, z_m) + R'_{st\ell} \,.$$

We do not give the remainder explicitly. Sufficient to say that since it contains a product of $\ell + 1$ ω-factors its sign is simply $(-1)^{\ell+1}$.

With t = 0, s varying, (2.19) is the Mayer-Montroll sequence. With s = 1, t varying, it is the Kirkwood-Salsburg sequence.

The Mayer-Montroll sequence has the form

$$(2.20) \qquad n_s = \sum_{0}^{\ell} z^s (-1)^m A_{sm} n_m + (-1)^{\ell+1} R_{s\ell} ,$$

with non-negative Asm and $R_{s\ell}$, and no z dependence in the Asm. The $\ell = 0$ term is

$$(2.21) \qquad n_s = z^s A_{so} - R_{so} ; \quad (n_o = 1)$$

the $\ell = 1$ term with n_1 from (2.21):

$$(2.22) \qquad n_s = z^s A_{so} - z^s A_{s1}(zA_{1o} - R_{1o}) + R_{s1} .$$

Next $\ell = 2$, with n_1 from (2.22) and n_2 from (2.21) etc. In this way an alternating sequence of upper and lower bounds is generated:

$$(2.23) \qquad \begin{aligned} n_s &\leq z^s A_{so} \\ &\geq z^s A_{so} - z^{s+1} A_{s1} A_{1o} \\ &\leq z^s A_{so} - z^{s+1} A_{s1} A_{1o} + z^{s+2}(A_{s1} A_{11} A_{1o} + A_{s2} A_{2o}), \end{aligned}$$

these being truncations of the full Mayer fugacity expansion.

3. Quantum Partition Functions and Distributions

The partition function for an N particle system obeying Maxwell-Boltzmann (classical) statistics is

$$(3.1) \qquad Z_N = \sum_i \int dx_1 \, .. \, dx_N \; \Phi_i^*(x_1 \, .. \, x_N) \, e^{-\beta H_N} \, \Phi_i(x_1 \, .. \, x_N)$$

$$(3.2) \qquad = \operatorname{tr} e^{-\beta H_N} ,$$

with no symmetry restrictions on the wave functions. The grand partition function is the same weighted average as (2.3):

$$(3.3) \qquad \mathfrak{Z} = \sum_{N=0}^{\infty} \frac{z^N}{N!} \operatorname{tr} e^{-\beta H_N} ,$$

but with $z = e^{\beta\mu}$ from here on. Alternatively, if a "thermal propagator" is defined,

$$(3.4) \qquad K_N(x_1 \, .. \, x_N \, \beta', y_1 \, ... \, y_N \, \beta'') =$$

$$= \sum_i \Phi_i^*(y_1 \, .. \, y_N) \Phi_i(x_1 \, .. \, x_N) \cdot \exp - E_{N,i}(\beta' - \beta'') \qquad \beta' \geq \beta''$$

$$K_N = 0 , \quad \beta' < \beta''$$

then (3.3) goes over into

$$(3.5)\quad \mathcal{Z} = \sum_{N=0} \frac{z^N}{N!} \int dx_1 \,..\, dx_N \, K_N(x_1 \,..\, x_N \,\beta, x_1 \,..\, x_N \,0) \,.$$

The designation "propagator" carries over from quantum mechanics where an identical function (except for $\beta \longrightarrow \frac{it}{\hbar}$) advances a wave function in time. (See also Section 4.)

The one particle propagator is

$$(3.6)\quad K(x\beta', y\beta'') = \sum_k \phi_k^*(y)\phi_k(x) \exp - E_k(\beta' - \beta'') \,.$$

Evaluating for free particles

$$(3.7)\quad K^o(x\beta', y\beta'') = \sum_k \frac{1}{V} \exp[ik(x - y) - \frac{\hbar^2 k^2}{2m}(\beta' - \beta'')]$$

$$= \left(\frac{m}{2\pi(\beta'-\beta'')\hbar^2}\right)^{3/2} \exp - \frac{m}{2\hbar^2}\frac{(x - y)^2}{(\beta'-\beta'')} \,,$$

with Fourier transform

$$(3.8)\qquad K^o(k, \beta' - \beta'') = \exp - \frac{\hbar^2 k^2}{2m}(\beta' - \beta'') \,.$$

If the particles are bosons (fermions) drop the N! and sum over distinct symmetric (antisymmetric) states in (3.1) or (3.4).

Immediate developments will not depend on the nature of the statistics. We define s-particle space-temperature distributions

$$(3.9)\quad n_s^{(j)}(x_1'\beta_1'x_2'\beta_2' \ldots x_n'\beta_n';x_{n+1}'\beta_{n+1}' \ldots ; \ldots ; \ldots x_s'\beta_s')$$

$$= \mathfrak{z}^{-1} \sum_{N=j} \frac{z^N}{(N-j)!} \operatorname{tr}[\exp(-\beta H_N)$$

$$: \delta(x_1(\beta_1') - x_1') \ldots \delta(x_1(\beta_n') - x_n')$$

$$\cdot\ \delta(x_2(\beta_{n+1}') - x_{n+1}') \ldots \delta(x_j(\beta_s') - x_s') :],$$

where the arguments are distributed consecutively into j groups set off by ; . The j labels particles 1 .. j. Within each group arguments refer to the same particle. If j = s for example, so that each group has one particle, the distribution is fully mutual. At the other extreme j = 1 and the distribution is fully self. Each δ-function is a Heisenberg operator

$$(3.10)\qquad \delta(x(\beta') - x') = \exp(\beta' H_N)\delta(x - x') \exp - \beta' H_N ,$$

and the : : orders these factors so that ones with larger β' are placed further to the left. In particular

$$(3.11)\quad n(x'\beta') = \mathfrak{z}^{-1} \sum_{1} \frac{z^N}{N!} N \operatorname{tr}(e^{-(\beta-\beta')H_N}\, \delta(x_1 - x')e^{-\beta' H_N}) ,$$

the density, a constant, n, for uniform systems,

$$(3.12)\quad n_2(x_1'\beta_1'x_2'\beta_2') = \mathfrak{z}^{-1} \sum_1 \frac{z^{N}_{N}}{N!} \operatorname{tr}\Big[e^{-(\beta-\beta_1')H_N}\, \delta(x_1 - x_1')\, e^{-(\beta_1'-\beta_2')H_N}\, \delta(x_1 - x_2') e^{-\beta_2' H_N} \Big] \qquad (\beta_1' > \beta_2')$$

the self pair distribution, and

$$(3.13)\quad n_2(x_1'\beta_1';x_2'\beta_2') = \mathfrak{z}^{-1} \sum_2 \frac{z^N}{N!} N(N-1) \operatorname{tr}\Big[e^{-(\beta-\beta_1')H_N}\, \delta(x_1 - x_1')\, e^{-(\beta_1'-\beta_2')H_N}\, \delta(x_2 - x_2') e^{-\beta_2' H_N} \Big] \qquad (\beta_1' > \beta_2'),$$

the mutual pair distribution. The physical pair distribution is (3.13) with $\beta_1' = \beta_2'$. At equal temperature arguments (3.12) becomes singular: $n\delta(x_1' - x_2')$.

We append to $\mathfrak{z}$ an external potential in the Heisenberg representation

$$(3.14)\quad \mathfrak{z}[U] \equiv \sum_0 \frac{z^N}{N!} \operatorname{tr} \exp(-\beta H_N) : \exp - \int_0^\beta \sum_{i=1}^{N} U(x_i(\beta'),\beta')d\beta' :^{*}$$

We can by this purely formal device generate quantum $\hat{n}_s$ and $\hat{F}_s$. Equations (2.7) and (2.8) generalize to

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* Note: (3.14) is to be regarded as in the interaction representation. All the U dependence is in the exponential. Equation (3.10) is still true, i.e. these operators have no U dependence.

$$(3.15)\quad \hat{n}(x_1\beta_1 \ldots x_s\beta_s)\mathcal{Z} = \frac{\delta \mathcal{Z}[U]}{-\delta U(x_1\beta_1)\ldots-\delta U(x_s\beta_s)}\Big|_{U=0},$$

$$(3.16)\quad \hat{n}(1) = n(1), \quad \hat{n}_2(12) = n_2(1;2) + n_2(12),$$

$$\hat{n}_3(123) = n_3(1;2;3) + n_3(1;23) + n_3(13;2) + n_3(12;3) + n_3(123), \ldots,$$

while

$$(3.17)\quad \hat{F}_s(x_1\beta_1 \ldots x_s\beta_s) = \frac{\delta \log \mathcal{Z}[U]}{-\delta U(x_1\beta_1)\ldots-\delta U(x_s\beta_s)}\Big|_{U=0},$$

$$(3.18)\quad \hat{F}_1 = \hat{n}_1, \quad \hat{F}_2 = \hat{n}_2 - \hat{n}\hat{n},$$

$$\hat{F}_3 = \hat{n}_3 - \sum \hat{n}_2\hat{n} + 2\hat{n}\hat{n}\hat{n}, \ldots,$$

generalize (2.11) and (2.12). To close this section some free particle functions are evaluated.

For classical statistics (3.5) becomes:

$$(3.19)\quad \mathcal{Z}^{o} = \sum_0 \frac{z^N}{N!}\int dx_1 \ldots dx_N \prod_{i=1}^{N} K^{o}(x_i\beta x_i 0)$$

$$= \sum_0 \frac{z^N}{N!}\left(\int dx\, K^{o}(x\beta x0)\right)^N$$

$$(3.20)\quad = \exp zV\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2},$$

by (3.6),

$$(3.20')\quad n^{o} = \frac{z}{V}\,\frac{\partial \log \mathcal{Z}^{o}}{\partial z} = z\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}.$$

The free particle self pair distribution from (3.12):

$$(3.21)\quad n_2^o = \mathfrak{z}^{o^{-1}} \left(\sum_1 \frac{z^N N}{N!} \operatorname{tr} e^{-\beta T_{N-1}}\right)$$

$$\operatorname{tr}\left(e^{-(\beta-\beta_1')T_1} \delta(x_1 - x_1') e^{-(\beta_1'-\beta_2')T_1} \delta(x_1 - x_2') e^{-\beta_2' T_1}\right),$$

which, inserting complete sets of states,

$$(3.22)\quad = z \sum_{i,j,k} < \Phi_i^* \mid e^{-(\beta-\beta_1')T_1} | \Phi_j > < \Phi_j^* \mid \delta(x_1 - x_1')$$

$$\cdot\ e^{-(\beta_1'-\beta_2')T_1} | \Phi_k > < \Phi_k^* \mid \delta(x_1 - x_2') e^{-\beta_2' T_1} | \Phi_i > ,$$

$$(3.23)\quad = z \int dx \sum_j \Phi_j^* (x_1') \Phi_j (x) e^{-(\beta-\beta_1')E_j}$$

$$\cdot \sum_k \Phi_k^* (x_2') \Phi_k (x_1') e^{-(\beta_1'-\beta_2')E_k}$$

$$\cdot \sum_i \Phi_i^* (x) \Phi_i (x_2') e^{-\beta_2' E_i} ,$$

$$(3.24)\quad = z \int dx\ K^o(x\beta, x_1'\beta_1') K^o(x_1'\beta_1', x_2'\beta_2') K^o(x_2'\beta_2', x0) .$$

Then, using (3.7) or (3.8) :

$$(3.25)\quad n_2^o\ (k, \beta_1-\beta_2) = n e^{-\frac{\hbar^2 k^2}{2m}\left(|\beta_1-\beta_2| - \frac{|\beta_1-\beta_2|^2}{\beta}\right)} .$$

An easy extension of (3.24) is:

$$(3.26)\quad n_s^{\circ}(x_1\beta_1 \ldots x_s\beta_s) = z\int dx\ K^{\circ}(x\beta x_1\beta_1)K^{\circ}(x_1\beta_1x_2\beta_2) \ldots K^{\circ}(x_s\beta_s x0)\ ,$$

free full self distributions, $(\beta > \beta_1 > \beta_2 > \ldots > \beta_s > 0)$.

The free functions for quantum statistics are postponed to a later section.

4. The Integral Representation

Refer back to the expression for the one particle thermal propagator, (3.6). If an arbitrary wave function $\psi(x,\beta)$ is defined by

$$(4.1)\qquad \psi(x\beta) = \sum_k c_k\ \phi_k(x)e^{-\beta E_k},$$

we see that K has the property

$$(4.2)\qquad \psi(x_2\beta_2) = \int_V K(x_2\beta_2x_1\beta_1)\psi(x_1\beta_1)dx_1\ .$$

Also from (3.6)

$$(4.3)\quad K(x_3\beta_3x_1\beta_1) = \int_V K(x_3\beta_3x_2\beta_2)K(x_2\beta_2x_1\beta_1)dx_2\ .$$

Consider now the following expression:

$$(4.4)\quad I = \left(\frac{m}{2\pi\varepsilon\hbar^2}\right)^{3/2} \int_{-\infty}^{\infty} \exp\left[-\frac{m}{2\hbar^2}\frac{(x_2-x_1)^2}{\varepsilon} - \varepsilon\phi(x_1)\right]\psi(x_1\beta_1)\,dx_1 \ ,$$

with ε a small quantity of units inverse energy (like β_1).

When x_2 is appreciably different from x_1 little is contributed to the integral. We therefore replace $x_1 - x_2$ by η, with the expectation that the main contribution to (4.4) occurs at small η,

$$(4.5)\quad I = \left(\frac{m}{2\pi\varepsilon\hbar^2}\right)^{3/2} \int_{-\infty}^{\infty} d\eta \, \exp\left[-\frac{m}{2\hbar^2}\frac{\eta^2}{\varepsilon} - \varepsilon\phi(x_2+\eta)\right] \cdot \psi(x_2+\eta,\beta_1) \ .$$

Dropping the η in the potential and expanding that term in ε, ψ in η:

$$(4.6)\quad I = \left(\frac{m}{2\pi\varepsilon\hbar^2}\right)^{3/2} \int d\eta \, \exp\left[-\frac{m}{2\hbar^2}\frac{\eta^2}{\varepsilon}\right](1-\varepsilon\phi(x_2)) \cdot \left(\psi(x_2\beta_1) + \eta\frac{\partial\psi}{\partial x_2} + \frac{1}{2}\eta^2\frac{\partial^2\psi}{\partial x_2^2}\right) \ ,$$

$$(4.7)\quad = (1-\varepsilon\phi(x_2))\psi(x_2\beta_1) + \frac{\hbar^2}{2m}\varepsilon\frac{\partial^2\psi}{\partial x_2^2} \ ,$$

dropping the smallest term. But

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x_2^2} + \phi(x_2)\right)\psi(x_2\beta_1) = -\frac{\partial\psi(x_2\beta_1)}{\partial\beta_1} \ ,$$

is Schrödinger's equation with the replacement

$\frac{it_1}{\hbar} \longrightarrow \beta_1$ so

$$(4.8) \quad I = \psi(x_2,\beta_1) + \varepsilon \frac{\partial\psi(x_2\beta_1)}{\partial\beta_1} = \psi(x_2,\beta_1 + \varepsilon) ,$$

to first order. Hence by (4.2) we identify

$$(4.9) \quad K(x_2\beta_1 + \varepsilon, x_1\beta_1) = \left(\frac{m}{2\pi\varepsilon\hbar^2}\right)^{3/2} \exp\left[- \frac{m}{2\hbar^2\varepsilon} (x_2 - x_1)^2 - \varepsilon\phi(x_1)\right].$$

Now by (M - 1) repeated application of (4.3), we arrive at the representation, with some notation changes

$$(4.10) \quad K(x\beta', y\beta'') = A^M \int_{-\infty}^{\infty} dx_{\beta_1} \cdots dx_{\beta_{M-1}}$$

$$\exp - \sum_{k=1}^{M} \varepsilon\left[\frac{m}{2\hbar^2} \dot{x}^2_{\beta_k} + \phi(x_{\beta_k})\right] ,$$

$\varepsilon \longrightarrow 0$, where the position of the particle at "time" β_k is denoted by x_{β_k}, $\beta_k - \beta_{k-1} = \varepsilon$, $\beta_M - \beta_o = M\varepsilon$,

$$(4.11) \quad \dot{x}_{\beta_k} = \frac{x_{\beta_k} - x_{\beta_{k-1}}}{\varepsilon} , \quad \beta_M = \beta', \quad \beta_o = \beta'' ,$$

$$A = \left(\frac{m}{2\pi\varepsilon\hbar^2}\right)^{3/2} , \quad x_{\beta'} = x, \quad x_{\beta''} = y .$$

This is the Feynman path integral form of the thermal propagator.

We may envision a particle traveling from y at "time" β'' to x at β' along a path marked off by the x_{β_k}; the path

is weighted by the exponential in (4.10) and all x_{β_k} are integrated over, except for the end points.

Equation (4.11) has the N particle generalization

$$(4.12)\quad K(x_1 \,..\, x_N\ \beta', y_1 \,..\, y_N\ \beta'') =$$

$$= A^{M\cdot N} \int dx_{1_{\beta_1}} \cdots dx_{N_{\beta_{M-1}}}$$

$$\exp - \sum_{k=1}^{M} \varepsilon \left[\sum_{i=1}^{N} \frac{m}{2\hbar^2} \dot{x}^2_{i_{\beta_k}} + \frac{1}{2} \sum_{i \neq j}^{N} \phi(x_{i_{\beta_k}} - x_{j_{\beta_k}}) \right] .$$

The integral representation of the Boltzmann grand partition function now follows from (3.5)

$$(4.13)\quad \mathfrak{z} = \sum_{0} \frac{z^N}{N!} A^{MN} \int dx_1 \,..\, dx_N \int dx_{1_{\beta_1}} \cdots dx_{N_{\beta_{M-1}}} \quad \exp - [\quad]$$

$$(4.14)\qquad \beta_M = \beta\ , \quad \beta_o = 0$$

$$x_{1_o} = x_{1_\beta} \equiv x_1,\ \ldots,\ x_{N_o} = x_{N_\beta} \equiv x_N\ .$$

Thus each Boltzmann particle returns to its starting place after "time" β.

In quantum statistics we must include paths in which the final configuration is some permutation of the original one, as the particles are indistinguishable [8].

If $(x_1,\ldots,x_N)$ denotes the original configuration,

$p(x_1 \ldots x_N)$ will denote the final one and

$$(4.15) \quad \mathfrak{z} = \sum_{N=0} \frac{z^N}{N!} A^{MN} \sum_p (\pm 1)^p \int dx_1 \ldots dx_N$$

$$\int_p dx_{1_{\beta_1}} \ldots dx_{N_{\beta_{M-1}}} \exp - [\quad] ,$$

$\int_p$ meaning a particular permutation described above. The + sign is for bosons, - for fermions.

To obtain distributions add an external potential

$$(4.16) \qquad U = \sum_{k=1}^{M} \varepsilon \sum_{i=1}^{N} U(x_{i_{\beta_k}}, \beta_k)$$

to $\mathfrak{z}$ and employ (3.15) - (3.18). We can then identify, for classical statistics,

$$(4.17) \quad n_s^{(j)}(x_1'\beta_1' \ldots x_n'\beta_n'; x_{n+1}'\beta_{n+1}' \ldots ; \ldots ; \ldots x_s'\beta_s')$$

$$= \mathfrak{z}^{-1} \sum_{N=j} \frac{z^N}{(N-j)!} A^{MN} \int dx_1 \ldots dx_N \int dx_{1_{\beta_1}} \ldots dx_{N_{\beta_{M-1}}}$$

$$\exp - [\quad]_{U=0} \cdot \delta(x_{1_{\beta_1'}} - x_1') \ldots \delta(x_{1_{\beta_n'}} - x_n')$$

$$\cdot \delta(x_{2_{\beta_{n+1}'}} - x_{n+1}') \ldots \delta(x_{j_{\beta_s'}} - x_s') ,$$

adding notation $\sum\limits_{p} (\pm 1)^p$, $\int_p$ in quantum statistics. See (3.9) and discussion following it.

Some examples:

(4.18) $$n(x'\beta') = \mathcal{Z}^{-1} \sum_{N=1} \frac{z^N}{(N-1)!} A^{MN} \int dx_1 \ldots dx_N$$

$$\int dx_{1_{\beta_1}} \ldots dx_{N_{\beta_{M-1}}} \exp - [\quad]_{U=0}$$

$$\cdot\ \delta(x_{1_{\beta'}} - x') ,$$

(4.19) $n_2(x'\beta'x''\beta'')$ ("self")

$$= \mathcal{Z}^{-1} \sum_{1} \frac{z^N}{(N-1)!} A^{MN} \int dx_1 \ldots dx_N$$

$$\int dx_{1_{\beta_1}} \ldots dx_{N_{\beta_{M-1}}} \exp - [\quad]_{U=0}$$

$$\delta(x_{1_{\beta'}} - x')\delta(x_{1_{\beta''}} - x'') ,$$

(4.20) $n_2(x'\beta';x''\beta'')$ ("mutual")

$$= \mathcal{Z}^{-1} \sum_{2} \frac{z^N}{(N-2)!} A^{MN} \int dx_1 \ldots dx_N \int dx_{1_{\beta_1}} \ldots dx_{N_{\beta_{M-1}}}$$

$$\exp - [\quad]_{U=0} \cdot \delta(x_{1_{\beta'}} - x')\delta(x_{2_{\beta''}} - x'') ,$$

adding the usual notation for quantum statistics. It is also true that, for all quantities expressed as path integrals,

$$(4.21) \quad \hat{n}_s(x_1\beta_1 \ldots x_s\beta_s|U)\mathfrak{z}[U] = \frac{\delta^s \mathfrak{z}[U]}{-\delta U(x_1\beta_1)\ldots -\delta U(x_s\beta_s)} ,$$

and

$$(4.22) \quad \hat{F}_s(x_1\beta_1 \ldots x_s\beta_s|U) = \frac{\delta^s \log \mathfrak{z}[U]}{-\delta U(x_1\beta_1)\ldots -\delta U(x_s\beta_s)} ,$$

with the U of (4.16).

The $\hat{n}_s$ have also the simple constructional definition

$$(4.23) \quad \hat{n}_s(x_1'\beta_1' \ldots x_s'\beta_s') = \mathfrak{z}^{-1} \sum_1 \frac{z^N}{N!} \int dx_1 \ldots dx_N$$

$$\int dx_{1_{\beta_1}} \ldots dx_{N_{\beta_{M-1}}} \exp - [\quad]$$

$$\rho(x_1'\beta_1') \ldots \rho(x_s'\beta_s')$$

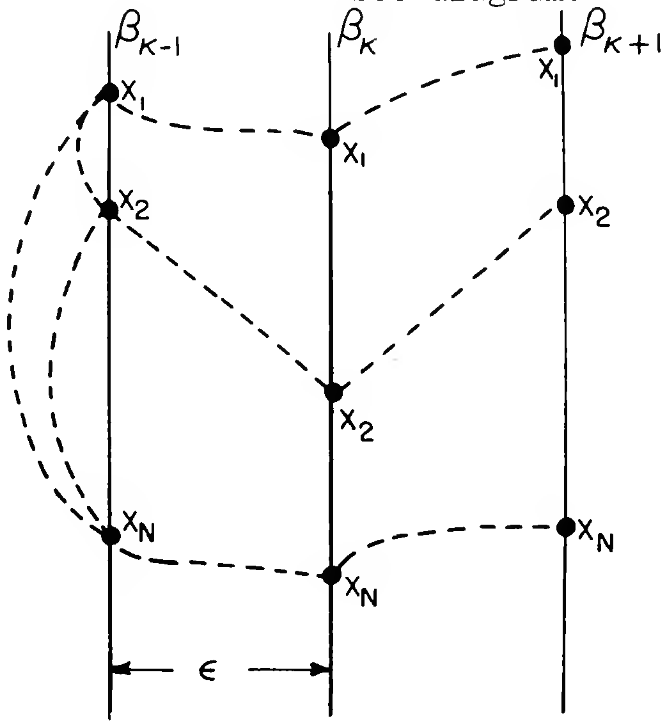
where

$$(4.24) \qquad \rho(x_k\beta_k) = \sum_{i=1}^{N} \delta(x_{i_{\beta_k}} - x_k) .$$

Since the external potential (4.16) is expressible as

$$(4.25) \qquad U = \sum_{k=1}^{M} \varepsilon \int dx_k \, \rho(x_k\beta_k) \, U(x_k\beta_k) ,$$

the truth of (4.21) is easily verified. Formulas like (4.13), (4.17) - (4.20) bear a resemblance to the corresponding expressions for classical mixtures, with the temperature index taking the place of species parameter. The interactions from the mixture point of view are somewhat peculiar, see (4.12), in that one of them involves particles of the same species only, while the other is nearest neighbor in species index, see (4.11). The resemblance is exploited in the final two sections. See diagram.



The interactions in the exponent of the path integral (4.12).

While we have so far taken expectations of coordinate operators only (δ-functions), the path integral representation easily accomodates momentum expectations. These will involve

full self distributions at infinitesimally separated temperature arguments. Thus for example,

$$(4.26)\qquad \left\langle \sum_{i=1}^{N} \frac{im}{\hbar}\, \dot{x}_{i_{\beta_k}} \right\rangle = \frac{m}{\hbar\varepsilon} \left\langle \sum_{i=1}^{N} (x_{i_{\beta_k}} - x_{i_{\beta_{k-1}}}) \right\rangle$$

$$= \mathcal{Z}^{-1} \sum_{0} \frac{z^N}{N!} A^{MN} \int dx_1 \,..\, dx_N \int dx_{1_{\beta_1}} \ldots dx_{N_{\beta_{M-1}}}$$

$$\exp - [\ \ ] \cdot \sum_{i=1}^{N} \frac{im}{\varepsilon\hbar} (x_{i_{\beta_k}} - x_{i_{\beta_{k-1}}})$$

$$(4.27)\qquad = \lim_{\varepsilon \to 0} \frac{im}{\hbar\varepsilon} \int dx dy\; n_2(x\beta_k y\beta_{k-1})(x - y) \;,$$

which is of course zero. One must be more careful with the kinetic energy expectation. Feynman shows [8] that

$$(4.28)\qquad - \sum_{i=1}^{N} \frac{m}{2\hbar^2\varepsilon^2} (x_{i_{\beta_{k+1}}} - x_{i_{\beta_k}})(x_{i_{\beta_k}} - x_{i_{\beta_{k-1}}})$$

has a finite expectation. This works out to

$$(4.29)\qquad \langle K.\ E. \rangle = - \lim_{\varepsilon \to 0} \frac{m}{2\hbar^2\varepsilon^2} \int dx dy dz (x - y)(y - z)$$

$$\cdot\; n_3(x\beta_{k+1}\; y\beta_k\; z\beta_{k-1}) \;.$$

5. Classical Statistics: Bootstrap Operation

From here on the integral representation will be used exclusively. Formulas (4.13), (4.17), (4.21) - (4.23) are basic.

In this section we derive relations between lower and higher distributions. The general idea is that a distribution defined for a system in which one or more particles are "fixed" is convertible by integrations into a higher order distribution. To "fix" a particle means to omit integrations over it at every point of its path. Most of these integrations are restored by the conversion process mentioned. This is a formal procedure. There are no recoil effects, the kinetic energy acting like a constant throughout.

By fixing a number of particles in the partition function <u>all</u> higher distributions may be obtained. Such a relation is the quantum analog of (2.15).

Let us write the partition function for a system in which j particles are fixed. These provide an external potential for the remaining N - j particles, thereby introducing a non-uniformity into $\mathcal{J}$,

$$(5.1)\quad \mathcal{Z}[U_\phi] = \sum_{N=j} \frac{N-j}{(N-j)!} \int dx_{j+1} \cdots dx_N \int dx_{j+1_{\beta_1}} \cdots dx_{N_{\beta_{M-1}}}$$

$$\cdot \exp - \varepsilon \frac{M}{k=1} \left[\sum_{i=1}^{j} \frac{m}{2h^2} \dot{x}^2_{i_{\beta_k}} + \sum_{i=j+1}^{N} \frac{m}{2\hbar^2} \dot{x}_{i_{\beta_k}} \right.$$

$$\left. + \frac{1}{2} \sum_{\substack{1\\ i\neq \ell}}^{j} \phi(x_{i_{\beta_k}} - x_{\ell_{\beta_k}}) + \frac{1}{2} \sum_{\substack{j+1\\ i\neq \ell}}^{N} \phi(x_{i_{\beta_k}} - x_{\ell_{\beta_k}}) \right]$$

$$\cdot \exp - \varepsilon \sum_{k=1}^{M} \sum_{i=j+1}^{N} U_\phi(x_{i_{\beta_k}}, \beta_k) ,$$

$$(5.2)\qquad U_\phi(x_{i_{\beta_k}}, \beta_k) = \sum_{\ell=1}^{j} \phi(x_{i_{\beta_k}} - x_{\ell_{\beta_k}}, \beta_k) ,$$

[cf. (2.13)]. For convenience the constant first and third terms in the exponential have been included. Now perform

$$(5.3)\qquad I^j_s \equiv \int dx_1 \cdot\cdot dx_j \int dx_{1_{\beta_1}} \cdots \int dx_{j_{\beta_{M-1}}}$$

$$\cdot\ \delta(x_{1_{\beta_1'}} - x_1')\delta(x_{1_{\beta_2'}} - x_2') \cdots \delta(x_{1_{\beta_n'}} - x_n')$$

$$\cdot\ \delta(x_{2_{\beta_{n+1}'}} - x_{n+1}') \cdots \delta(x_{j_{\beta_s'}} - x_s') ,$$

each δ eliminating an integration. The <u>canonical</u> part transforms, by (4.17):

$$(5.4)\quad I_s^j \frac{Z^{N-j}[U_\phi]}{(N-j)!} = n_s^{N(j)}(x_1'\beta_1' \,..\, x_n'\beta_n';\ x_{n+1}'\beta_{n+1}' \,\ldots;\ \ldots;$$

$$\ldots\ x_s'\beta_s')\ \frac{Z^N}{N!} \quad .$$

Multiply through by z^N and sum $\sum_{N=j}^{\infty}$:

$$(5.5)\quad z^j I_s^j\, \mathcal{Z}[U_\phi] = n_s^{(j)}(x_1'\beta_1' \,..\, x_n'\beta_n';\ x_{n+1}'\beta_{n+1}' \,\ldots;\ \ldots$$

$$\ldots;\ \ldots\ x_s'\beta_s')\,\mathcal{Z}\ .$$

This is the analog of (2.15). The final distribution which we get on the right of (5.5) is, of course, for a uniform system.

Some special cases of (5.5):

(a) j = s, which means one integration is stopped per particle,

$$(5.6)\quad z^j \int dx_1 \,..\, dx_j \int dx_{1_{\beta_1}} \ldots \int dx_{j_{\beta_{M-1}}}\, \delta(x_{1_{\beta_1'}} - x_1')\,\delta(x_{2_{\beta_2'}} - x_2')\ldots$$

$$\delta(x_{j_{\beta_j'}} - x_j')\,\mathcal{Z}[U_\phi] = n_j(x_1'\beta_1';\ x_2'\beta_2';\ \ldots;\ x_j'\beta_j')\,\mathcal{Z}\ ,$$

a completely mutual distribution.

(b) j = 1, one particle fixed,

$$(5.7)\quad z \int dx_1 \int dx_{1_{\beta_1}} \ldots dx_{1_{\beta_{M-1}}}\, \delta(x_{1_{\beta_1'}} - x_1')\ldots\delta(x_{1_{\beta_s'}} - x_s')\,\mathcal{Z}[U_\phi]$$

$$= n_s(x_1'\beta_1' x_2'\beta_2' \,\ldots\, x_s'\beta_s')\,\mathcal{Z},$$

a full self distribution.

(c) with $s = 2$ in (5.6) and (5.7), we have formulas for the mutual and self pair distribution respectively.

Suppose we had begun with, in place of (5.1),

$$(5.8)\quad n_t^{(k)}(x_1'' \beta_1'' \ldots x_n'' \beta_n'' ; x_{n+1}''\beta_{n+1}'' \ldots ; \ldots ; \ldots x_t'' \beta_t'' | U_\phi)_{\mathfrak{z}}[U_\phi]$$

$$= \sum_{N=j+k} \frac{z^{N-j}}{(N-j-k)!} \int dx_{j+1} \ldots dx_{j+k} \ldots dx_N$$

$$\int dx_{j+1_{\beta_1}} \ldots dx_{N_{\beta_{M-1}}} \exp - \varepsilon \sum_{k=1}^{M} \Bigg[\sum_{i=1}^{j} \frac{m}{2\hbar^2} \dot{x}^2_{i_{\beta_k}}$$

$$+ \sum_{i=j+1}^{N} \frac{m}{2\hbar^2} \dot{x}^2_{i_{\beta_k}} + \frac{1}{2} \sum_{\substack{1 \\ i \neq \ell}}^{j} \phi(x_{i_{\beta_k}} - x_{\ell_{\beta_k}})$$

$$+ \frac{1}{2} \sum_{\substack{j+1 \\ i \neq \ell}}^{N} \phi(x_{i_{\beta_k}} - x_{\ell_{\beta_k}}) \Bigg] \cdot \exp - \varepsilon \sum_{k=1}^{M} \sum_{i=j+1}^{N} U_\phi(x_{i_{\beta_k}}, \beta_k)$$

$$\cdot\ \delta(x_{j+1_{\beta_1''}} - x_1'') \ldots \delta(x_{j+1_{\beta_n''}} - x_n'') \delta(x_{j+2_{\beta_{n+1}''}} - x_{n+1}'') \ldots$$

$$\delta(x_{j+k_{\beta_t''}} - x_t''),$$

where the arguments $1,\ldots,t$ are consecutively distributed among k groups set off by ; (particles $j+1,\ldots j+k$), and

with particles 1 .. j fixed, supplying U_ϕ, as before.

Then if (5.3) is applied to (5.8),

$$(5.9)\quad z^j I_s^j\, n_t^{(k)}(x_1'' \beta_1'' \ldots x_n'' \beta_n'' ; x_{n+1}'' \beta_{n+1}'' \ldots ; \ldots ;$$

$$\ldots x_t'' \beta_t'' |U_\phi)_{\mathfrak{z}}[U_\phi]$$

$$= n_{s+t}^{(j+k)}(x_1'\beta_1' \ldots x_n'\beta_n' ; x_{n+1}'\beta_{n+1}' \ldots ; \ldots ; \ldots x_s' \beta_s' ;$$

$$x_1'' \beta_1'' \ldots x_n'' \beta_n'' ; x_{n+1}''\beta_{n+1}'' \ldots ; \ldots ; \ldots x_t'' \beta_t'')_{\mathfrak{z}} ,$$

which is the generalization of (2.14).

Example: $j = 1$, $s = 1$, $k = 1$ and $t = 1$,

$$(5.10)\quad z \int dx_1 \int dx_{1_{\beta_1}} \ldots dx_{1_{\beta_{M-1}}}\, \delta(x_{1_{\beta_1'}} - x_1')\, n_1(x_1'' \beta_1'' |U_\phi)_{\mathfrak{z}}[U_\phi]$$

$$= n_2(x_1'\beta_1' ; x_1'' \beta_1'')_{\mathfrak{z}} ,$$

the mutual pair distribution.

In addition to (5.5) and (5.10) separate formulas can be derived for the $\hat{n}_s$.

To see this write the canonical partition function for a system of N particles in an external potential:

$$(5.11)\quad Z^N[U] = \int dx_1 \ldots dx_N \int dx_{1_{\beta_1}} \ldots dx_{N_{\beta_{M-1}}}$$

$$\exp - \varepsilon \sum_{k=1}^{M} \Big[\sum_1^j \frac{m}{2\hbar^2} \dot{x}^2_{i_{\beta_k}} + \sum_{j+1}^{N} \frac{m}{2\hbar^2} \dot{x}^2_{i_{\beta_k}}$$

$$+ \frac{1}{2} \sum_1^{j}{}' \phi(x_{i_{\beta_k}} - x_{\ell_{\beta_k}}) + \frac{1}{2} \sum_{j+1}^{N}{}' \phi(x_{i_{\beta_k}} - x_{\ell_{\beta_k}})$$

$$+ \sum_1^j \sum_{j+1}^{N} \phi(x_{i_{\beta_k}} - x_{\ell_{\beta_k}}) + \sum_1^N U(x_{i_{\beta_k}}, \beta_k) \Big]$$

$$(5.12)\quad = \int dx_1 \ldots dx_j \int dx_{1_{\beta_1}} \ldots dx_{j_{\beta_{M-1}}} Z^{N-j}[U + U_\phi]$$

$$\exp - \varepsilon \sum_{k=1}^{M} \Big[\sum_1^j \frac{m}{2\hbar^2} \dot{x}^2_{i_{\beta_k}} + \frac{1}{2} \sum_1^{j}{}' \phi(x_{i_{\beta_k}} - x_{\ell_{\beta_k}})$$

$$+ \int dx_k\, \zeta(x_k \beta_k) U(x_k \beta_k) \Big] ,$$

$$(5.13)\quad \zeta(x_k \beta_k) = \sum_1^j \delta(x_{i_{\beta_k}} - x_k) ,$$

with U_ϕ as in (5.2).

Differentiating both sides s times with respect to U, using (4.21),

$$(5.14)\quad \hat{n}_s^N(x_1'\beta_1' \ldots x_s'\beta_s'|U)Z^N[U]$$

$$= \int dx_1 \ldots dx_j \int dx_{1_{\beta_1}} \ldots dx_{j_{\beta_{M-1}}} \exp [\quad]_U$$

$$\sum_{t=0}^{s} \zeta(x_1'\beta_1') \ldots \zeta(x_t'\beta_t')\hat{n}_{s-t}^{N-j}(x_{t+1}'\beta_{t+1}' \ldots x_s'\beta_s'|U + U_\phi)$$

$$\cdot\ Z^{N-j}[U + U_\phi] \frac{s!}{(s-t)!t!} \quad .$$

Taking $s = j = 1$ for example,

$$(5.15)\quad \hat{n}_1^N(x_1'\beta_1'|U)Z^N[U]$$

$$= \int dx_1 \int dx_{1_{\beta_1}} \ldots dx_{1_{\beta_{M-1}}} \exp - \varepsilon \sum_{k=1}^{M} \Big[\frac{m}{2\hbar^2} \dot{x}_{1_{\beta_k}}^2$$

$$+ U(x_{1_{\beta_k}}, \beta_k)\Big] \cdot \Big[\zeta(x_1'\beta_1')Z^{N-1}[U + U_\phi]$$

$$+ \hat{n}_1^{N-1}(x_1'\beta_1'|U + U_\phi)Z^{N-1}[U + U_\phi]\Big] \quad ,$$

this, by (4.23), (4.24) and (5.13),

$$= \int dx_1 \int dx_{1_{\beta_1}} \ldots dx_{1_{\beta_{M-1}}} \exp - [\quad]_U$$

$$\cdot\ N\delta(x_{1_{\beta_1'}} - x_1')Z^{N-1}[U + U_\phi] \quad ,$$

which goes over into grand canonical form

$$(5.16)\quad \hat{n}_1(x_1'\beta_1'|U)\mathfrak{Z}[U] = z\int dx_1 \int dx_{1_{\beta_1}} \dots dx_{1_{\beta_{M-1}}} \exp\,[\quad]_U$$

$$\delta(x_{1_{\beta_1'}} - x_1')\mathfrak{Z}[U + U_\phi]\ ,$$

which, except for U, is (5.5) with j = s = 1.

With j = 1, s = 2

$$(5.17)\quad \hat{n}_2^N(x_1'\beta_1'x_2'\beta_2'|U)Z^N[U]$$

$$= \int dx_1 \int dx_{1_{\beta_1}} \dots dx_{1_{\beta_{M-1}}} \exp -\,[\quad]_U$$

$$\Big[\zeta(x_1'\beta_1')\zeta(x_2'\beta_2')Z^{N-1}[U + U_\phi]$$

$$+ \zeta(x_1'\beta_1')\hat{n}_1^{N-1}(x_2'\beta_2'|U + U_\phi)Z^{N-1}[U + U_\phi]\cdot 2$$

$$+ \hat{n}_2^{N-1}(x_1'\beta_1'x_2'\beta_2'|U + U_\phi)Z^{N-1}[U + U_\phi]\Big]$$

$$= \int dx_1 \int dx_{1_{\beta_1}} \dots dx_{1_{\beta_{M-1}}} \exp -\,[\quad]_U$$

$$\Big[N\delta(x_{1_{\beta_1'}} - x_1')\delta(x_{1_{\beta_2'}} - x_2')Z^{N-1}[U + U_\phi]$$

$$+ N\delta(x_{1_{\beta_1'}} - x_1')\hat{n}_1^{N-1}(x_2'\beta_2'|U + U_\phi)Z^{N-1}[U + U_\phi]\Big]\ ,$$

$$(5.18)\quad \hat{n}_2(x_1'\beta_1'x_2'\beta_2'|U)\mathfrak{Z}[U]$$

$$= z\int dx_1 \int dx_{1_{\beta_1}} \cdots dx_{1_{\beta_{M-1}}} \exp - [\quad]_U$$

$$\cdot \Big[\delta(x_{1_{\beta_1'}} - x_1')\delta(x_{1_{\beta_2'}} - x_2')\mathfrak{Z}[U + U_\phi]$$

$$+ \delta(x_{1_{\beta_1'}} - x_1')\hat{n}_1(x_2'\beta_2'|U + U_\phi)\mathfrak{Z}[U + U_\phi]\Big] ,$$

on the grand ensemble.

To summarize, we have in this section found relations between lower order distribution with external potentials (due to fixed particles) and higher distributions for uniform systems. The main results are embodied in (5.5), (5.9) and (5.14). These relations will now be applied to the problem of obtaining integral equations and bounds for distributions.

6. Bounds on Distributions

We shall require in this and later sections a functional Taylor expansion. Consider a function of space and temperature arguments $\omega(x\beta)$ which changes from initial to final value due to a change in a parameter α, α varying from 0 to 1:

$$(6.1)\quad \omega(x\beta,\alpha) = \omega_o(x\beta) + \alpha[\omega(x\beta) - \omega_o(x\beta)] .$$

Given a functional of $\omega(x\beta)$, $\psi[\omega(x\beta)]$, we wish to expand it in the deviation of ω from its initial value. Since ψ can be regarded as a function of α through (6.1), the Taylor expansion for it, including remainder is just:

$$(6.2) \quad \psi(\alpha)_{\alpha=1} = \sum_{j=0}^{s} \frac{1}{j!} \frac{\partial \psi^j(\alpha)}{\partial \alpha^j} \bigg|_{\alpha=0} + \int_0^1 \frac{\partial^{s+1}\psi(\alpha)}{\partial \alpha^{s+1}} \frac{(1-\alpha)^s}{s!} \, d\alpha$$

Since by the chain rule:

$$(6.3) \quad \frac{\partial}{\partial \alpha} = \int \frac{\partial \omega(x\beta,\alpha)}{\partial \alpha} \frac{\delta}{\delta \omega(x\beta,\alpha)} \, dx d\beta \,,$$

$$(6.4) \quad = \int \Delta\omega(x\beta) \frac{\delta}{\delta\omega(x\beta,\alpha)} \, dx d\beta \,, \quad (\Delta\omega = \omega - \omega_o) \,,$$

the functional expansion is

$$(6.5) \quad \psi[\omega(x\beta)] = \psi[\omega_o(x\beta)] + \sum_{j=1}^{s} \frac{1}{j!} \int \cdots \int \Delta\omega(x_1\beta_1) \cdots \Delta\omega(x_j\beta_j)$$

$$\cdot \frac{\delta^j \psi[\omega]}{\delta\omega(x_1\beta_1)\cdots\delta\omega(x_j\beta_j)} \bigg|_{\omega=\omega_o} dx_1 d\beta_1 \cdots dx_j d\beta_j$$

$$+ \int_o^1 \frac{(1-\alpha)^s}{s!} \int \cdots \int \Delta\omega(x_1\beta_1) \cdots \Delta\omega(x_{s+1}\beta_{s+1})$$

$$\cdot \frac{\delta^{s+1}\psi[\omega(\alpha)]}{\delta\omega(x_1\beta_1\alpha)\cdots\delta\omega(x_{s+1}\beta_{s+1}\alpha)} dx_1 d\beta_1 \cdots dx_{s+1} d\beta_{s+1} d\alpha$$

For example, if $\omega(x\beta) = U(x\beta)$, $\psi[\omega] = \mathfrak{z}[U]$, and $\omega_o = 0$, we have

$$(6.6)\quad \mathfrak{z}[U] = \mathfrak{z}[0] + \sum_{j=1}^{s} \frac{(-1)^j}{j!} \int dx_1 d\beta_1 \,..\, dx_j d\beta_j \,\mathfrak{z}[0]$$

$$\cdot\ \hat{n}_j(x_1\beta_1 \,..\, x_j\beta_j) U(x_1\beta_1) \,..\, U(x_j\beta_j)$$

$$+ \int_0^1 \int dx_1 d\beta_1 \,..\, dx_{s+1} d\beta_{s+1} d\alpha \,\frac{(1-\alpha)^s}{s!} (-1)^{s+1}$$

$$\cdot\ \mathfrak{z}[0] \hat{n}_{s+1}(x_1\beta_1 \,..\, x_{s+1}\beta_{s+1}, \alpha) U(x_1\beta_1) .. U(x_{s+1}\beta_{s+1}),$$

in which (4.21) has been used.

Of particular interest is the case of purely repulsive potential U. Then, since the $\hat{n}_j$ are positive, the jth term in the series has the sign $(-1)^j$, while the remainder has the sign $(-1)^{s+1}$. The series alternates and successive upper and lower bounds may be iterated out:

$$\begin{aligned}(6.7)\quad \mathfrak{z}[U] &\le \mathfrak{z}[0] \\ &\ge \mathfrak{z}[0] - \int dx_1 d\beta_1 \hat{n}(x_1\beta_1) \mathfrak{z}[0] U(x_1\beta_1) \\ &\le \mathfrak{z}[0] - \int dx_1 d\beta_1 \hat{n}(x_1\beta_1) \mathfrak{z}[0] U(x_1\beta_1) \\ &\qquad + \frac{1}{2} \int dx_1 d\beta_1 dx_2 d\beta_2 \hat{n}_2(x_1\beta_1 x_2\beta_2) \mathfrak{z}[0] U(x_1\beta_1) U(x_2\beta_2) \ .\end{aligned}$$

If we specialize the U to the pair potential arising from t fixed particles at $y_1 \,..\, y_t$,

$$(6.8)\qquad U_\phi(x_1\beta_1) = \sum_{i=1}^{t} \phi(x_1 - y_{i_{\beta_1}}, \beta_1) \ ,$$

bounds on uniform distributions may be obtained. For example, if $t = 1$, by (5.16),

$$(6.9)\quad \hat{n}_1(y_1\beta_1) \le \hat{n}_1^{\circ}(y_1\beta_1)$$

$$\ge \hat{n}_1^{\circ}(y_1\beta_1) - \int d\hat{x}\,d\bar{x}_1\,d\bar{\beta}_1\,\hat{n}_1^{\circ}(\bar{x}_1\bar{\beta}_1)$$

$$\cdot\ \phi(\bar{x}_1 - \hat{x})\,n_2^{\circ}(\hat{x}\bar{\beta}_1 y_1\beta_1)\ ,$$

or with $t = 1$ and $t = 2$, by (5.5) and (5.16),

$$(6.10)\quad \hat{n}_2(y_1\beta_1 y_2\beta_2) \le \hat{n}_2^{\circ}(y_1\beta_1 y_2\beta_2)$$

$$\ge \hat{n}_2^{\circ} - \int d\hat{x}\,d\bar{x}_1\,d\bar{\beta}_1\,\hat{n}_1^{\circ}(\bar{x}_1\bar{\beta}_1)$$

$$\cdot\ \phi(\bar{x}_1 - \hat{x})\Big[n_3^{\circ}(\hat{x}\bar{\beta}_1 y_1\beta_1 y_2\beta_2)$$

$$+\ n_2^{\circ}(\hat{x}\bar{\beta}_1 y_1\beta_1)\hat{n}_1^{\circ}(y_2\beta_2)$$

$$+\ \hat{n}_1^{\circ}(y_1\beta_1)n_2^{\circ}(\hat{x}\bar{\beta}_1 y_2\beta_2)\Big]\ .$$

(The interaction between fixed particles [$t = 2$] has been neglected.) This is the beginning of a Mayer-Montroll type sequence. Once the $\hat{n}$ are known the individual distributions may be found by the equations of Section 5.

If (6.6) is differentiated t times,

$$(6.11)\quad \hat{n}_t(x_1'\beta_1' \,..\, x_t'\beta_t'|U)\mathfrak{z}[U] =$$

$$= \hat{n}_t\mathfrak{z}[0] + \sum_{j=1}^{s} \frac{(-1)^j}{j} \int dx_1 d\beta_1 \,..\, dx_j d\beta_j \mathfrak{z}[0]$$

$$\cdot\ \hat{n}_{t+j}(x_1'\beta_1' \,..\, x_t'\beta_t',\ x_1\beta_1 \,..\, x_j\beta_j)$$

$$\cdot\ U(x_1\beta_1) \,..\, U(x_j\beta_j)$$

$$+ \int_0^1 \int dx_1 d\beta_1 \,..\, dx_{s+1} d\beta_{s+1} d\alpha \frac{(1-\alpha)^s}{s!} (-1)^{s+1}$$

$$\mathfrak{z}[0]\hat{n}_{t+s+1}(x_1'\beta_1' \,..\, x_t'\beta_t',\ x_1\beta_1 \,..\, x_{s+1}\beta_{s+1},\alpha)$$

$$U(x_1\beta_1) \,..\, U(x_{s+1}\beta_{s+1}) ,$$

and, for example, choosing t = 1,

$$(6.12)\quad \hat{n}_1(x_1'\beta_1'|U)\mathfrak{z}[U] \leq \hat{n}_1(x_1'\beta_1')\mathfrak{z}[0]$$

$$\geq \hat{n}_1(x_1'\beta_1')\mathfrak{z}[0]$$

$$- \int dx_1 d\beta_1 \mathfrak{z}[0]\hat{n}_2(x_1'\beta_1' x_1\beta_1)U(x_1\beta_1) .$$

Specializing U by fixing one particle,

$$(6.13)\quad U_\phi(x_1\beta_1) = \phi(x_1 - y_{1_{\beta_1}}, \beta_1),$$

and using (5.18), [also (6.9)],

$$(6.14)\quad \hat{n}_2(x_1'\beta_1'y_1\beta_1) \leq \hat{n}_2^o$$

$$\geq \hat{n}_2^o - \int d\hat{x}d\bar{x}_1 d\bar{\beta}_1 \phi(\bar{x}_1 - \hat{x})$$

$$\cdot \Big[\hat{n}_1^o(x_1'\beta_1')n_2^o(\hat{x}\bar{\beta}_1 y_1\beta_1)\hat{n}_1^o(\bar{x}_1\bar{\beta}_1)$$

$$+ n_3^o(\hat{x}\bar{\beta}_1 x_1'\beta_1' y_1\beta_1)\hat{n}_1^o(\bar{x}_1\bar{\beta}_1)$$

$$+ \hat{n}_2^o(x_1'\beta_1'\bar{x}_1\bar{\beta}_1)n_2^o(\hat{x}\bar{\beta}_1 y_1\beta_1)\Big] .$$

This with (6.9) is the beginning of a Kirkwood-Salsburg type sequence.

7. Classical Statistics: Debye-Hückel Sequence; Direct Correlation.

In Classical Statistical Mechanics it is possible to derive a general, self-consistent sequence of integral equations for the modified Ursell functions $\hat{F}_s$ [7]. The simplest of these is the linearized Debye-Huckel equation (2.17). Unfortunately this procedure cannot be generalized to quantum mechanics because the quantum $\hat{F}_s$, (4.22), do not satisfy bootstrap operations of the kind developed in Section 5. We therefore confine ourselves to the pair distribution. We seek a consistent approximation for the self and mutual distributions.

Expand $\log \mathfrak{z}[U_\phi]$ v. U_ϕ where $\mathfrak{z}[U_\phi]$ given by (5.1) $j = 1$ and

$$U_\phi(x_{i_{\beta_k}}, \beta_k) = \phi(x_{i_{\beta_k}} - x_{1_{\beta_k}}, \beta_k) \quad , \tag{7.1}$$

particle "1" fixed.

The functional Taylor expansion is:

$$\begin{aligned}
\log \mathfrak{z}[U_\phi] &= \log \mathfrak{z}[0] + \int_0^\beta d\bar{\beta} d\bar{x} \left. \frac{\delta \log \mathfrak{z}[U_\phi]}{\delta U_\phi(\bar{x}\bar{\beta})} \right|_{U_\phi = 0} U_\phi(\bar{x}\bar{\beta}) \\
&+ \frac{1}{2!} \int_0^\beta d\bar{\beta} d\bar{x} d\hat{\beta} d\hat{x} \left. \frac{\delta^2 \log \mathfrak{z}[U_\phi]}{\delta U_\phi(\bar{x}\bar{\beta}) \delta U_\phi(\hat{x}\hat{\beta})} \right|_{U_\phi = 0} \\
&\cdot U_\phi(\bar{x}\bar{\beta}) U_\phi(\hat{x}\hat{\beta}) + \ldots \quad .
\end{aligned} \tag{7.2}$$

$$\begin{aligned}
&= \log \mathfrak{z}[0] - \int_0^\beta d\bar{\beta} d\bar{x} \, n_1(\bar{x}\bar{\beta}) \phi(\bar{x} - x_{1_{\bar{\beta}}}, \bar{\beta}) \\
&+ \frac{1}{2} \int_0^\beta d\bar{\beta} d\bar{x} d\hat{\beta} d\hat{x} [n_2(\bar{x}\bar{\beta};\ \hat{x}\hat{\beta}) + n_2(\bar{x}\bar{\beta}\hat{x}\hat{\beta}) \\
&- n_1(\bar{x}\bar{\beta}) n_1(\hat{x}\hat{\beta})] \\
&\cdot \phi(\bar{x} - x_{1_{\bar{\beta}}}, \bar{\beta}) \phi(\hat{x} - x_{1_{\hat{\beta}}}, \hat{\beta}) \quad ,
\end{aligned} \tag{7.3}$$

in which use has been made of (4.22) and (3.18).

Differentiating (7.3):

$$(7.4)\quad n_1[x''\beta''|U_\phi] = n_1(x''\beta'') - \int_0^\beta d\bar{x}d\bar{\beta}(n_2(x''\beta''\,;\,\bar{x}\bar{\beta}) + n_2(x''\beta''\bar{x}\bar{\beta}) - n_1(x''\beta'')n_1(\bar{x}\bar{\beta})) \cdot \phi(\bar{x} - x_{1_{\bar{\beta}}},\bar{\beta})\ .$$

Linearizing (7.3) and dropping an inessential term linear in U_ϕ:

$$(7.5)\quad \mathfrak{z}[U_\phi] = \mathfrak{z}[0] + \frac{1}{2}\int_0^\beta d\bar{\beta}d\bar{x}d\hat{\beta}d\hat{x}\mathfrak{z}[0] (n_2(\bar{n}\bar{\beta};\ \hat{x}\hat{\beta}) + n_2(\bar{x}\bar{\beta}\hat{x}\hat{\beta}) - n^2)\phi(\bar{x} - x_{1_{\bar{\beta}}},\bar{\beta})\phi(\hat{x} - x_{1_{\hat{\beta}}},\hat{\beta})\ .$$

Applying (5.7): $(j = 2,4)$

$$(7.6)\quad n_2(x'\beta'x''\beta'') = n_2^o(x'\beta'x''\beta'') + \frac{1}{2}\int_0^\beta d\bar{\beta}d\bar{x}d\hat{\beta}d\hat{x}d\tilde{x}d\check{x} (n_2(\bar{x}\bar{\beta};\ \hat{x}\hat{\beta}) + n_2(\bar{x}\bar{\beta}\hat{x}\hat{\beta}) - n^2) \cdot \phi(\bar{x} - \tilde{x})\phi(\hat{x} - \check{x}) \cdot n_4^o(x'\beta'x''\beta''\tilde{x}\bar{\beta}\check{x}\hat{\beta})\ ,$$

the n_4^o being a completely self 4 particle distribution. "o" denotes free particles.

Applying (5.10) and (5.7) (with $j = 1,2$) to (7.4),

after one has multiplied through by $z\mathfrak{z}[U_\phi]$,

$$(7.7)\quad n_2(x'\beta';\ x''\beta'') = n^2 - \int_0^\beta d\overline{\beta}d\overline{x}d\hat{x}(n_2(x''\beta'';\ \overline{x}\overline{\beta}) + n_2(x''\beta''\overline{x}\overline{\beta}) - n^2)\phi(\overline{x} - \hat{x})\, n_2(x'\beta'\hat{x}\overline{\beta})\ .$$

Equations (7.6), (7.7) are consistent simultaneous integral equations for $n_2(\ )$ and $n_2(;)$, valid for sufficiently weak potential.

A cruder approximation, which has the virtue of being exactly solvable, is to replace $n_2(\ )$ by its free value in (7.7):

$$(7.8)\quad \overline{n}(x'\beta';\ x''\beta'') = -\int_0^\beta d\overline{\beta}d\overline{x}d\hat{x}(\overline{n}(x''\beta'';\ \overline{x}\overline{\beta}) + n_2^0(x''\beta''\overline{x}\overline{\beta}))\phi(\overline{x} - \hat{x}) \cdot n_2^0(x'\beta'\hat{x}\overline{\beta})\ ,$$

$$\overline{n}(;) = n_2(;) - n^2.$$

The solution of (7.8) proceeds as follows.

The Fourier transform of (7.8),

$$(7.9)\quad \overline{n}(k,\beta'\beta'') = -\int_0^\beta d\overline{\beta}(\overline{n}(k,\beta''\overline{\beta}) + n_2^0(k,\beta''\overline{\beta}))\phi(k)n_2^0(k,\overline{\beta}\beta')\ ,$$

has for kernel of the homogeneous equation

$$(7.10) \quad n_2^o(k,\bar{\beta}\beta') = n \exp - \frac{\hbar^2 k^2}{2m} \left(|\beta' - \bar{\beta}| - \frac{|\beta'-\bar{\beta}|^2}{\beta}\right) ,$$

see (3.25).

This kernel has the property that

$$(7.11a) \quad n_2^o(k,\beta - \alpha) = n_2^o(k,\alpha) ,$$

$$\alpha = |\beta' - \bar{\beta}|$$

and we define, for temperatures $> \beta$,

$$(7.11b) \quad n_2^o(k,\beta + \alpha) = n_2^o(k,\alpha) .$$

It then follows easily that

$$(7.12) \quad \bar{n}(k,\beta'\beta'') = \sum_n \frac{\lambda_n^2}{\lambda-\lambda_n} \phi_n^*(\beta'')\phi_n(\beta') ,$$

where

$$(n = \pm \text{ int}, 0.)$$

$$(7.13) \qquad \lambda_n(k) = \int_0^\beta d\alpha \; n_2^o(k,\alpha) \exp \frac{2\pi i n\alpha}{\beta} ,$$

$$(7.14) \qquad \phi_n(\beta') = \beta^{-1/2} \exp - \frac{2\pi i n\beta'}{\beta} ,$$

and

$$(7.15) \qquad \lambda = - \frac{1}{\phi(k)} .$$

The λ_n and ϕ_n being eigenvalues and eigenfunctions of the kernel. Once the pair distribution is known one can work

backwards to find $\mathfrak{z}$ and hence the thermodynamics. This is done by recognizing that if

$$\phi \longrightarrow \gamma\phi \quad , \qquad 0 \leq \gamma \leq 1$$

(7.16) $$\frac{d \log \mathfrak{z}(\gamma)}{d\gamma} = - \frac{\beta}{\gamma} < \gamma\phi >_{\gamma} ,$$

(7.17) $$\log \mathfrak{z}(1) = \log \mathfrak{z}^{o} - \beta \int_0^1 \frac{d\gamma}{\gamma} <\gamma\phi>_{\gamma} .$$

Since, setting $\beta' = \beta''$ in (7.12)

(7.18) $$<\phi> = \frac{1}{2} (2\pi)^{-3} V \int dk \, n_2 \underset{(\text{mutual})}{(k)} \phi(k) ,$$

we arrive at, by (7.12), (7.17) and (7.18),

(7.19) $$\log \mathfrak{z} = \log \mathfrak{z}^{o} + \frac{1}{2} (2\pi)^{-3} V \int dk \sum_n \Big[\phi(k)\lambda_n - \log(1 + \phi(k)\lambda_n)\Big] .$$

This is the result obtained by Montroll and Ward in their theory of the election gas [10].

At high temperatures, $\beta \longrightarrow 0$,

$$\lambda_n \longrightarrow n_1 \beta \delta_{no} ,$$

(7.20) $$\bar{n}(k) = - \frac{n^2 \beta\phi(k)}{1+n\beta\phi(k)} ,$$

which is also the solution of (2.17), and gives rise to the Debye-Hückel equation of state for a screened Coulomb potential (neutralizing background) [2], [10].

Equation (7.8) is the quantum generalization of (2.17).

Returning to classical statistical mechanics momentarily we recall that

$$(7.21) \qquad \frac{\delta n(x|U)}{-\delta\beta U(y)} = n(x|U)\delta(x - y) + n_2(x,y|U) - n(x|U)n(y|U) \ ,$$

is composed of a direct effect at y due to U(y) plus a longer range reaction. Let us consider the inverse derivative (which will have meaning on a grand ensemble where arbitrary density variations can be made) and split it into singular and non-local parts:

$$(7.22) \qquad \frac{-\delta\beta U(y)}{\delta n(x|U)} \equiv \frac{\delta(x-y)}{n(x|U)} - c(x,y|U) \ .$$

$c(x,y|U)$ is called the direct correlation function [1], the name to become clearer presently. The derivatives in (7.21) and (7.22) are matrix inverses of one another and therefore

$$(7.23) \qquad \int \frac{\delta n(x|U)}{-\delta\beta U(y)} \, \frac{-\delta\beta U(y)}{\delta n(z|U)} \, dy = \delta(x - z) \ .$$

Substituting (7.21) and (7.22) into (7.23)

$$(7.24) \qquad g(x,y) - 1 = c(x,y) + \int c(x,z)n(z)(g(z,y) - 1)dz ,$$

where

$$(7.25) \qquad g(x,y) = \frac{n_2(x,y)}{n(x)n(y)}$$

(the presence of U is understood).

Equation (7.24) when iterated becomes

$$(7.26) \qquad g(x,y) - 1 = c(x,y) + \int c(x,z)n(z)c(z,y)dz$$

$$+ \int c(x,z)n(z)c(z,\omega)n(\omega)c(\omega,y)dz d\omega$$

$$+ \ldots ,$$

i.e. $g - 1$ is represented by a "direct correlation" from x to y plus a sum over all the ways direct correlations can be transmitted via intermediate particles from x to y at density n.

One expects that c will have a shorter range than $g - 1$, of the order of the interparticle potential. (The non-interacting g is unity). In fact, for hard cores c has exactly the range of the potential [9].

Consider again the Debye-Hückel equation (2.17). Here

$$(7.27) \qquad (g - 1)(k) = - \frac{\beta\phi(k)}{1+n\beta\phi(k)} . \quad [7.20]$$

In general, from (7.24), U = 0,

$$(7.28) \qquad (g - 1)(k) = \frac{c(k)}{1-nc(k)} ,$$

so that in this case

$$c(k) = -\beta\phi(k) , \tag{7.28'}$$

the potential itself. Knowledge of c supplies the thermodynamics, for as may be shown [11] ($U = 0$),

$$\beta \frac{\partial p}{\partial n} = 1 - n \int c(x)dx , \tag{7.29}$$

p = grand canonical pressure, $= \log \mathfrak{Z}(V\beta)^{-1}$

In an attempt to generalize these ideas to quantum systems we have first, in matrix notation,

$$\frac{\delta n}{-\delta U} = n_2(\quad) + n_2(;) - nn , \tag{7.30}$$

((4.22) with s = 2) .

The inverse derivative

$$-\frac{\delta U}{\delta n} \equiv n_2^{-1}(\quad) - c , \tag{7.31}$$

with n_2^{-1} the matrix inverse of the self distribution, which at equal temperatures is $\frac{\delta(x'-x'')}{n}$, and

$$\frac{\delta n}{-\delta U} \cdot \frac{-\delta U}{\delta n} = 1 . \tag{7.32}$$

Substituting (7.30) and (7.31) into (7.32) we have for uniform systems (U = 0),

$$\overline{n} = \overline{n}\, c\, n_2 + n_2\, c\, n_2 \ , \tag{7.33}$$

$$\overline{n} = n_2(;) - n^2 \quad .$$

It is convenient to replace c by $n_2^{-1}\, c'\, n_2^{-1}$, leading to:

$$\overline{n} = c + \overline{n}\, n_2^{-1}\, c \ , \tag{7.34}$$

dropping the prime.

This iterates in the fashion of (7.26)

$$\overline{n} = c + c\, n_2^{-1}\, c + c\, n_2^{-1}\, c\, n_2^{-1}\, c + \ldots \quad . \tag{7.35}$$

The thermodynamic relation can be shown to be

$$\beta \frac{\partial p}{\partial n} = 1 - \frac{n}{\beta} \int_0^{\beta} dx d\alpha \, \frac{c(x,\alpha)}{n^2} \quad . \tag{7.36}$$

As an illustration, consider (7.8). There

$$n_2^o(k,\beta'\beta'') = \sum_n \lambda_n \, \phi_n^*(\beta'')\phi_n(\beta') \ , \tag{7.37}$$

so that

$$n_2^{o^{-1}}(k,\beta'\beta'') = \sum_n \lambda_n^{-1} \, \phi_n^*(\beta'')\phi_n(\beta') \ , \tag{7.38}$$

and

$$\overline{n}(k,\beta'\beta'') = \sum_n \frac{\lambda_n^2}{\lambda-\lambda_n} \, \phi_n^*(\beta'')\phi_n(\beta') \ . \tag{7.39}$$

The Fourier transformed equation (7.34) is

$$(7.40) \quad \bar{n}(k,\beta'\beta'') = c(k,\beta'\beta'') + \int_0^\beta \bar{n}(k,\beta'\bar{\beta})n_2^{-1}(k,\bar{\beta}\hat{\beta}) \cdot c(k,\hat{\beta}\beta'')d\bar{\beta}d\hat{\beta} .$$

Making the substitutions (7.38) and (7.39) one identifies

$$(7.41) \quad c(k,\beta'\beta'') = \sum_n \frac{\lambda_n^2}{\lambda} \phi_n^*(\beta'')\phi_n(\beta') .$$

The classical limit of this is of course (7.28').

8. Quantum Statistics: Toron Decomposition; Bootstrap Operation

In this section relations like those of section five will be developed for the Einstein-Bose and Fermi-Dirac cases. We confine ourselves to one- and two-particle distributions only. We wish to relate, for example, the one-particle distribution in external potential due to fixed particles to the pair distribution for a uniform system.

Before this can be done it is necessary to rewrite $\mathfrak{z}$ and the distributions in forms which display the permutational sum in a way convenient to our purposes. These new forms also permit easy calculation of free particle functions. Recall that

$$(8.1) \qquad \mathcal{Z} = \sum_{N=0} \frac{Z^N}{N!} \sum_p (\pm)^p \int dx_1 \, .. \, dx_N \int_p dx_{1_{\beta_1}} \, .. \, dx_{N_{\beta_{M-1}}}$$

$$\exp - \sum_{k=1}^{M} \varepsilon \left[\sum_{i=1}^{N} \frac{m}{2\hbar^2} \dot{x}^2_{i_{\beta_k}} + \frac{1}{2} \sum_{i \neq j} \phi(x_{i_{\beta_k}} - x_{j_{\beta_k}}) \right] ,$$

[4.15] .

(Normalization factors are omitted for convenience in writing.) Consider

$$(8.2) \qquad Z_N = \sum_p (\pm)^p \int dx_1 \, .. \, dx_N \int_p dx_{1_{\beta_1}} \, .. \, dx_{N_{\beta_{M-1}}} \cdot \exp - [\ ] .$$

From these permutations, we extract a "closed loop" of t particles interacting with the remainder, $t \geq N$

$$\text{closed loop} \equiv \oint dx_{1_{\beta_1}} \, .. \, dx_{t_{\beta_{M-1}}}$$

means $\quad x_{1_o} = x_{t_\beta}, \quad x_{2_o} = x_{1_{\beta_1}}, \ \ldots$

$\qquad x_{t_o} = x_{t-1_\beta},$ i.e. particle one returns to its starting place after "time" $t\beta$. In the language of Montroll and Ward [10] this is a t particle toron. There are $N(N-1) \ldots (N-(t-1)) \cdot \frac{1}{N}$ ways to construct such a loop, the $\frac{1}{N}$ factor eliminating redundancies. This much of Z_N now appears as

$$(8.3)\quad \sum_p (\pm)^p \int dx_1 \ldots dx_N \, (\pm)^{t+1} \oint dx_{1_{\beta_1}} \ldots dx_{t_{\beta_{M-1}}}$$

$$\cdot \frac{N!}{(N-t)!} \, \frac{1}{N} \cdot \int_p dx_{t+1_{\beta_1}} \ldots dx_{N_{\beta_{M-1}}} \quad \exp - [\ ]\ ,$$

the permutation sum operating now only on particles $t + 1,\ldots,N$. The end points are as usual $x_{1_o} \equiv x_1, \ldots, x_{t_o} \equiv x_t, \ldots, x_{N_o} \equiv x_N$. The full Z_N includes a sum over all sizes of torons $t = 1,\ldots N$. So that

$$(8.4)\quad \mathfrak{z} = 1 + \sum_{N=1}^{\infty} \frac{Z^N}{N} \sum_{t=1}^{N} \frac{(\pm)^{t+1}}{(N-t)!} \sum_p (\pm)^p$$

$$\cdot \int dx_1 \ldots dx_N \oint dx_{1_{\beta_1}} \ldots dx_{t_{\beta_{M-1}}}$$

$$\cdot \int_p dx_{t+1_{\beta_1}} \ldots dx_{N_{\beta_{M-1}}} \quad \exp - [\ ]\ .$$

Reversing the order of the N and t sums with $N - t \longrightarrow s$, we have finally

$$(8.5)\quad \mathfrak{z} = 1 + \sum_{t=1}^{\infty} \sum_{s=0}^{\infty} \frac{Z^{s+t}}{(s+t)s!} (\pm)^{t+1} \sum_p (\pm)^p$$

$$\cdot \int dy_1 \ldots dy_t \oint dy_{1_{\beta_1}} \ldots dy_{t_{\beta_{M-1}}}$$

$$\cdot \int dx_1 \ldots dx_s \int_p dx_{1_{\beta_1}} \ldots dx_{s_{\beta_{M-1}}}$$

$$\cdot \exp - \varepsilon \sum_{k=1}^{M} \Bigg[\sum_{1}^{t} \frac{m}{2\hbar^2} \dot{y}^2_{i_{\beta_k}} + \sum_{1}^{s} \frac{m}{2\hbar^2} \dot{x}^2_{i_{\beta_k}} + \frac{1}{2} \sum_{1}^{s}{}' \phi(x_{i_{\beta_k}} - x_{j_{\beta_k}})$$

$$+ \frac{1}{2} \sum_{1}^{t}{}' \phi(y_{i_{\beta_k}} - y_{j_{\beta_k}}) + \sum_{1}^{t} \sum_{1}^{s} \phi(y_{i_{\beta_k}} - x_{j_{\beta_k}}) \Bigg] .$$

The third term in the potential is the toron interaction with the rest of the system. The second term is the toron self interaction.

In a similar fashion this toron decomposition may be accomplished for n_1, $n_2(\ )$ and $n_2(;)$ or alternatively these expressions may be derived from (8.5) by differentiation with respect to U.

We record the results:

$$(8.6) \quad n_1(x'\beta') = \mathfrak{Z}^{-1} \sum_{t=1} \sum_{s=0} \frac{Z^{s+t}}{s!} \sum_{p} (\pm)^{p+t+1}$$

$$\int dy_1 \ldots dy_t \oint dy_{1_{\beta_1}} \ldots dy_{t_{\beta_{M-1}}}$$

$$\int dx_1 \ldots dx_s \int_p dx_{1_{\beta_1}} \ldots dx_{s_{\beta_{M-1}}} \exp-[\ ] ,$$

$$\delta(y_{1_{\beta'}} - x') ,$$

$$(8.7) \quad n_2(x'\beta'x''\beta'') = \mathfrak{Z}^{-1} \sum_{t=1} \sum_{s=0} \frac{Z^{s+t}}{s!} \sum_{p} (\pm)^{p+t+1}$$

$$\int \ldots \int \exp - [\ ]\ \delta(y_{1_{\beta'}} - x')\delta(y_{1_{\beta''}} - x'') ,$$

and

$$(8.8)\quad n_2(x'\beta';x''\beta'') = z^{-1} \sum_{t=1} \sum_{s=1} \frac{Z^{s+t}s}{s!} \sum_p (\pm)^{p+t+1}$$

$$\int \cdots \int \exp - [\ ]\cdot\delta(y_{1_{\beta'}} - x')\delta(x_{1_{\beta''}} - x'')$$

$$+ z^{-1} \sum_{t=2} \sum_{s=0} \frac{Z^{s+t}}{s!} \sum_p (\pm)^{p+t+1}$$

$$\int \cdots \int \exp - [\ ] \cdot \sum_{i=2}^{t} \delta(y_{1_{\beta'}} - x')\delta(y_{i_{\beta''}} - x'')\ .$$

Formulas (8.6) - (8.8) give a relatively easy way of calculating free distributions,

$$(8.9)\quad n_1^o(x'\beta') = \sum_{t=1} (\pm)^{t+1}\ z^t \int dy_1 \cdots dy_t$$

$$\oint dy_{1_{\beta_1}} \cdots dy_{t_{\beta_{M-1}}} \cdot \delta(y_{1_{\beta'}} - x')$$

$$\exp - \varepsilon \sum_{k=1}^{M} \sum_{i=1}^{t} \frac{m}{2\hbar^2} \dot{y}^2_{i_{\beta_k}}\quad ,$$

but by (4.10) this is

$$(8.10)\quad n_1^o(x'\beta') = \sum_{t=1}^{\infty} (\pm)^{t+1}\ z^t \int K^o(y_1\beta y_t 0)K^o(y_t\beta y_{t-1}0)\cdots$$

$$\cdots K^o(y_2\beta x'\beta')K^o(x'\beta' y_1 0)$$

$$dy_1 \cdots dy_t\ ,$$

$$(8.11) \qquad = \sum_{t=1}^{\infty} (\pm)^{t+1} \frac{z^t}{t^{3/2}} \lambda ,$$

by (3.7) or (3.8),

$$\lambda = \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2} .$$

Since

$$n_1 = \frac{z}{V} \frac{\partial \log \mathfrak{z}}{\partial z} ,$$

$$(8.12) \qquad \log \mathfrak{z}^0 = V \sum_1 (\pm)^{t+1} \frac{z^t}{t^{5/2}} \lambda .$$

Similarly

$$(8.13) \quad n_2^0(x'\beta'x''\beta'') = \sum_1 (\pm)^{t+1} z^t \int dy_1 \ldots dy_t$$

$$(\beta' > \beta'') \qquad K^0(y_1\beta y_t 0)K^0(y_t\beta y_{t-1}0) \ldots$$

$$K^0(y_\alpha\beta x'\beta')K^0(x'\beta'x''\beta'')K^0(x''\beta''y_1 0) ,$$

$$(8.14) \quad n_2^0(k,\alpha) = \sum_{t=1} (\pm)^{t+1} \frac{z^t}{t^{3/2}} \lambda e^{-a\alpha + \frac{a\alpha^2}{\beta t}} ,$$

$$a = \frac{\hbar^2 k^2}{2m} , \quad \alpha = |\beta' - \beta''| ,$$

and

$$(8.15) \quad n_2^0(x'\beta';x''\beta'') - n^2 = \overline{n}^0$$

$$= \sum_{t=2} (\pm)^{t+1} z^t \sum_{i=2}^{t} \int dy_1 \ldots dy_t$$

$$(\beta' > \beta'') \qquad \cdot\, K^o(y_1\beta y_t 0) \ldots K^o(y_{i+1}\beta x'\beta')$$

$$\cdot\, K^o(x'\beta' y_i 0) \ldots K^o(y_2\beta x''\beta'')$$

$$\cdot\, K^o(x''\beta'' y_1 0) ,$$

(8.16) $\bar{n}^o(k,\alpha)$

$$= \sum_{t=2} (\pm)^{t+1} \frac{z^t}{t^{3/2}} \lambda \sum_{\ell=1}^{t-1} e^{-a(\beta\ell+\alpha)+a\frac{(\beta\ell+\alpha)^2}{\beta t}} .$$

As a check on (8.16) transform back into x space at $\alpha = 0$:

$$(8.17) \quad \bar{n}^o(x,0) = \sum_{t=2}^{\infty} \sum_{\ell=1}^{t-1} (\pm)^{t+1} \frac{z^t \lambda^2}{t^{3/2}(\ell - \frac{\ell^2}{t})^{3/2}} \exp - \left[\frac{x^2 \pi \lambda^{2/3}}{\ell - \frac{\ell^2}{t}}\right]$$

Redefining indices $t - \ell \longrightarrow m$,

$$(8.18) \quad \bar{n}^o(x,0) = \sum_{m=1}^{\infty} \sum_{\ell=1}^{\infty} \frac{z^{m+\ell}}{(m\ell)^{3/2}} (\pm)^{m+\ell+1} \lambda^2$$

$$\exp\,[-\, x^2 \pi \lambda^{2/3}(\ell^{-1} + m^{-1})]$$

$$= \pm\, \lambda^2 \left[\sum_{m=1}^{\infty} \frac{z^m}{m^{3/2}} (\pm)^m \exp\,(-\, x^2\pi\lambda^{2/3} m^{-1})\right]^2$$

the familiar London-Placzek formula.

One other free particle function will be included here for future reference: the free modified Ursell functions, $\hat{F}^o_s$,

$$(8.19)\quad \hat{F}_s^o(x_1\beta_1 \ldots x_s\beta_s)$$

$$= \sum_{t=1}^{\infty} (\pm)^{t+1} z^t \int dy_1 \ldots dy_t \oint dy_{1_{\beta_1}} \ldots dy_{t_{\beta_{M-1}}}$$

$$\exp - \varepsilon \sum_{k=1}^{M} \sum_{i=1}^{t} \frac{m}{2\hbar^2} \dot{y}^2_{i_{\beta_k}}$$

$$\sum_{i_1 \ldots i_{s-1}=1}^{t} \delta(y_{1_{\beta_1}} - x_1)\delta(y_{i_{1_{\beta_2}}} - x_2) \ldots \delta(y_{i_{s-1_{\beta_s}}} - x_s) .$$

(Montroll's "interaction propagator.") [12]

One of them, $\hat{F}_2^o$, we already have by summing (8.14) and (8.16):

$$(8.20)\quad F_2^o(k,\alpha) = \sum_{t=1}^{\infty} (\pm)^{t+1} \frac{z^t}{t^{3/2}} \lambda \sum_{\ell=0}^{t-1} e^{-a(\beta\ell+\alpha) + \frac{a(\beta\ell+\alpha)^2}{\beta t}} .$$

Let us now write the partition function (8.1) for a system in which a t-particle toron has been fixed:

$$(8.21)\quad \mathcal{Z}_t[U_\phi] = \sum_{s=0}^{\infty} \frac{z^s}{s!} \sum_p (\pm)^p \int dx_1 \ldots dx_s$$

$$\int_p dx_{1_{\beta_1}} \ldots dx_{s_{\beta_{M-1}}} \exp - \sum_{k=1}^{M} \varepsilon \Bigg[\sum_1^t \frac{m}{2\hbar^2} \dot{y}^2_{i_{\beta_k}}$$

$$+ \sum_1^s \frac{m}{2\hbar^2} \dot{x}^2_{i_{\beta_k}} + \frac{1}{2} \sum_1^{s}{}' \phi(x_{i_{\beta_k}} - x_{j_{\beta_k}})$$

$$+ \frac{1}{2} \sum_1^{t}{}' \phi(y_{i_{\beta_k}} - y_{j_{\beta_k}})$$

$$+ \sum_{i=1}^{s} \sum_{j=1}^{t} \phi(x_{i_{\beta_k}} - y_{j_{\beta_k}}, \beta_k) \Bigg] ,$$

including two constant terms (first and fourth) in $y_1 \ldots y_t$, and U_ϕ is the last term in the bracket. Then, according to (8.6) and (8.7):

$$(8.22)\quad \sum_{t=1}^{\infty} z^t (\pm)^{t+1} \int dy_1 \ldots dy_t \oint dy_{1_{\beta_1}} \ldots dy_{t_{\beta_{M-1}}}$$

$$\mathcal{J}_t[U_\phi]\delta(y_{1_{\beta'}} - x')\delta(y_{1_{\beta''}} - x'')$$

$$= n_2(x'\beta'x''\beta'')\mathfrak{z},$$

and

$$(8.23)\quad \sum_{t=1}^{\infty} z^t (\pm)^{t+1} \int dy_1 \ldots dy_t \oint dy_{1_{\beta_1}} \ldots dy_{t_{\beta_{M-1}}}$$

$$\mathcal{J}_t[U_\phi]\delta(y_{1_{\beta'}} - x') = n_1(x'\beta')\mathfrak{z}.$$

Similarly writing the density:

$$(8.24)\quad n_{1_t}(x''\beta''|U_\phi)\mathcal{J}_t[U_\phi]$$

$$= \sum_{s=1}^{\infty} \frac{z^s}{s!}\ s \sum_p (\pm)^p \int dx_1 \ldots dx_s \int_p dx_{1_{\beta_1}} \ldots dx_{s_{\beta_{M-1}}}$$

$$\exp -\varepsilon\Big[\sum_1^t \frac{m}{2\hbar^2} \dot{y}^2_{i_{\beta_k}} + \sum_1^s \frac{m}{2\hbar^2} \dot{x}^2_{i_{\beta_k}}$$

$$+ \frac{1}{2}\sum_1^{s}{}' \phi(x_{i_{\beta_k}} - x_{j_{\beta_k}}) + \frac{1}{2}\sum_1^{t}{}' \phi(y_{i_{\beta_k}} - y_{j_{\beta_k}})$$

$$+ \sum_{i=1}^{s}\sum_{j=1}^{t} \phi(x_{i_{\beta_k}} - y_{j_{\beta_k}}, \beta_k)\Big] \cdot \delta(x_{1_{\beta''}} - x''),$$

equation (8.8) implies:

$$(8.25)\quad \sum_{t=1}^{\infty} z^t(\pm)^{t+1} \int dy_1 \ldots dy_t \oint dy_{1_{\beta_1}} \ldots dy_{t_{\beta_{M-1}}}$$

$$n_{1_t}(x''\beta''|U_\phi)\mathfrak{z}_t[U_\phi]\delta(y_{1_{\beta'}} - x')$$

$$+ \sum_{t=2}^{\infty} z^t \;(\pm)^{t+1} \int dy_1 \ldots dy_t \oint dy_{1_{\beta_1}} \ldots dy_{t_{\beta_{M-1}}}$$

$$\mathfrak{z}_t[U_\phi] \sum_{i=2}^{t} \delta(y_{1_{\beta'}} - x')\delta(y_{i_{\beta''}} - x'') = n_2(x'\beta';x''\beta'')\mathfrak{z}\,.$$

Equations (8.22) and (8.23) convert the partition function to the self pair distribution and density respectively, while (8.25) requires both partition function and density to convert to the mutual pair distribution. In any case these equations are the "bootstrap operations" we set out to find.

In the next section, the last devoted to path integral methods, we apply these results to obtain a Debye-Hückel equation in quantum statistics.

We shall for convenience call the second term in (8.25) $\tilde{n}(x'\beta'x''\beta'')\mathfrak{z}$, that is,

$$(8.26)\quad \sum_{t=2}^{\infty} z^t \;(\pm)^{t+1} \int dy_1 \ldots dy_t \oint dy_{1_{\beta_1}} \ldots dy_{t_{\beta_{M-1}}}$$

$$\mathfrak{z}_t[U_\phi] \sum_{i=2}^{t} \delta(y_{1_{\beta'}} - x')\delta(y_{i_{\beta''}} - x'') \equiv \tilde{n}(x'\beta'x''\beta'')\mathfrak{z}\,.$$

For free particles (compare (8.8), second term),

$$(8.27)\qquad \tilde{n}^o = \bar{n}^o = n_2^o(;) - n^2\,.$$

9. Quantum Statistics: Debye-Hückel Sequence

Expand $\log \mathcal{Z}_t[U_\phi]$ v. U_ϕ, where $\mathcal{Z}_t[U_\phi]$ is given by (8.19), and

$$(9.1)\quad U_\phi(x_{i_{\beta_k}}, \beta_k) = \sum_{j=1}^{t} \phi(x_{i_{\beta_k}} - y_{j_{\beta_k}}, \beta_k) \; :$$

$$(9.2)\quad \log \mathcal{Z}_t[U_\phi] = \log \mathcal{Z}_t[0] - \int_0^\beta d\bar{\beta}\; d\bar{x}\; n_1 \sum_{j=1}^{t} \phi(x - y_{j_{\bar{\beta}}}, \bar{\beta})$$

$$+ \frac{1}{2}\int_0^\beta d\bar{\beta} d\bar{x} d\hat{\beta} d\hat{x} \left[n_2(\bar{x}\bar{\beta};\hat{x}\hat{\beta}) + n_2(\bar{x}\bar{\beta}\hat{x}\hat{\beta}) - n_1^2\right]$$

$$\cdot \sum_{i,j=1}^{t} \phi(\bar{x} - y_{j_{\bar{\beta}}}, \bar{\beta})\phi(\hat{x} - y_{i_{\hat{\beta}}}, \hat{\beta}) + \ldots \quad .$$

Differentiating (9.2),

$$(9.3)\quad n_{1_t}(x''\beta''|U_\phi) = n_1 - \int_0^\beta d\bar{x} d\bar{\beta} \left[n_2(x''\beta'';\bar{x}\bar{\beta})\right.$$

$$\left. + n_2(x''\beta''\bar{x}\bar{\beta}) - n_1^2\right] \sum_{j=1}^{t} \phi(\bar{x} - y_{j_{\bar{\beta}}}, \bar{\beta}) \; .$$

Linearizing (9.2) and dropping the linear term in ϕ:

$$(9.4)\quad \mathcal{Z}_t[U_\phi] = \mathcal{Z}_t[0] + \frac{1}{2}\int_0^\beta d\bar{\beta} d\bar{x} d\hat{\beta} d\hat{x}\; \mathcal{Z}_t[0] \left[n_2(\bar{x}\bar{\beta};\hat{x}\hat{\beta})\right.$$

$$\left. + n_2(\bar{x}\bar{\beta}\hat{x}\hat{\beta}) - n_1^2\right]$$

$$\sum_{i,j=1}^{t} \phi(\bar{x} - y_{j_{\bar{\beta}}}, \bar{\beta})\phi(\hat{x} - y_{i_{\hat{\beta}}}, \hat{\beta}) \; .$$

Applying (8.22) and (8.26), neglecting the t-toron self interaction on the right hand side of (9.4):

$$(9.5)\quad n_2(x'\beta'x''\beta'') + \tilde{n}(x'\beta'x''\beta'') = (n_2 + \bar{n})^{\circ}$$
$$+\frac{1}{2}\int_0^{\beta} d\bar{\beta}d\bar{x}d\hat{\beta}d\hat{x}d\tilde{x}d\hat{x}[n_2(\bar{x}\bar{\beta}\hat{x}\hat{\beta}) + \tilde{n} + \bar{n} - \tilde{n}]\phi(\bar{x} - \tilde{x})\phi(\hat{x} - \check{x})$$
$$\cdot\ \hat{F}_4^{\circ}(x'\beta'x''\beta''\tilde{x}\bar{\beta}\check{x}\hat{\beta})\ .$$

(See (8.19) for $\hat{F}_s^{\circ}$.)

Multiplying (9.3) by $\mathfrak{z}_t[U_\phi]$ and applying (8.22), (8.23), (8.25) and (8.26):

$$(9.6)\quad \bar{n}(x'\beta'x''\beta'') - \tilde{n}$$
$$= -\int_0^{\beta} d\bar{x}d\bar{\beta}d\hat{x}[\bar{n}(x''\beta''\bar{x}\bar{\beta}) - \tilde{n} + n_2 + \tilde{n}]\phi(\bar{x} - \hat{x})$$
$$\cdot(n_2(x'\beta'\hat{x}\bar{\beta}) + \tilde{n})\ .$$

Equations (9.5) and (9.6) are simultaneous, consistent integral equations for $\bar{n} - \tilde{n}$, $n_2 + \tilde{n}$. The $\tilde{n}$ itself is to a first approximation $\bar{n}^{\circ}$.

Just as in Section 7, we examine a simpler approximation, which is (9.6) with $n_2 + \tilde{n}$ replaced by its free particle value. But then (9.6) has the same form as (7.8) with kernel for the homogeneous equation

$$(9.7)\qquad (n_2 + \tilde{n})^{\circ} = \hat{F}_2^{\circ}\ .$$

This kernel, given by (8.20), has the properties

$$(9.8a)\qquad \hat{F}_2^o(k,\beta-\alpha) = \hat{F}_2^o(k,\alpha)$$

and

$$(9.8b)\qquad \hat{F}_2^o(k,\beta+\alpha) \equiv \hat{F}_2^o(k,\alpha) .$$

Then immediately

$$(9.9)\qquad \overline{n}(k,\beta'\beta'') - n = \sum_n \frac{\lambda_n^2}{\lambda-\lambda_n} \phi_n^*(\beta'')\phi_n(\beta') ,$$

with

$$(9.10)\qquad \lambda_n = \int_0^\beta d\alpha\ \hat{F}_2^o(k,\alpha)\ \exp 2\pi i n \frac{\alpha}{\beta} ;$$

ϕ_n and λ are the same as in Section 7.

This is again the Montroll and Ward result [10]. Equation (7.19) holds with the new λ_n. The fermion solution at low temperatures leads to the Gell-Mann-Brückner equation for the correlation energy (Coulomb) of the ground state.

10. The Potential Ensemble

The final three sections of this work are devoted to an alternate approach to finding integral equations for the pair distribution. As we did earlier, we will introduce the main ideas by working with the simpler formalism of classical statistical mechanics, then generalize.

Consider the classical grand partition function for a system with interparticle potential ϕ and external potential U

$$(10.1)\qquad \mathcal{J}[\phi|U] = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int dx_1 \ldots dx_N$$

$$\exp - \beta\left[\frac{1}{2}\sum_{i,j}{}' \phi(x_i - x_j) + \sum_{i}^{N} U(x_i)\right] .$$

We will allocate the potential ϕ to an external potential ψ which uses the particles as sources

$$(10.2)\qquad \psi(x) = \sum_{j=1}^{N} \phi(x - x_j)$$

$$(10.3)\qquad = \int dy\ \phi(xy)\rho(y) ,$$

where

$$(10.4)\qquad \rho(x) = \sum_{j=1}^{N} \delta(x - x_j) .$$

If K(xy) is the matrix inverse of ϕ,

$$(10.5)\qquad \int K(xy)\ \phi(yz)dy = - \delta(x - z) ,$$

where the negative sign makes K positive definite for attractive potentials, (10.3) inverts to

$$(10.6)\qquad \int K(xy)\ \psi(y)dy + \rho(x) = 0 .$$

The potential energy now assumes the form

$$(10.7) \quad \frac{1}{2}\sum_{i,j}{}' \phi(x_i - x_j) = \int dx\ \rho(x)\ \psi(x) + \frac{1}{2}\int dxdy\ K(xy)\psi(x)\psi(y) \ ,$$

apart from a self term.

We anticipate that the partition function can be rewritten as a functional integral over field amplitudes $\{\psi(x)\}$, i.e.

$$(10.8) \quad Z_N[\phi|U] = \frac{\int dx_1 \ldots dx_N \iint D\psi(x)\ \exp(-\beta\sum_1^N \psi(x_i) - \beta\sum_1^N U(x_i)) \cdot \exp(-\frac{\beta}{2}\int K(xy)\psi(x)\psi(y))dxdy}{\iint D\psi(x)\ \exp(-\frac{\beta}{2}\int K(xy)\psi(x)\psi(y))dxdy}$$

when $\iint D\psi(x)$ is suitably interpreted. The pure field contribution existing in the absence of particles has been divided out.

That (10.8) does indeed represent Z_N can be shown using only properties of translational invariance and positivity of the functional integrals [9]. The meaning of these integrals depends upon the choice of interparticle potential (and boundary conditions) in a particular problem. Thus, for example, a one dimensional Coulomb gas, neutralization at origin, leads to a Feynman path integral [9].

Equation (10.8) says that the additional potential ϕ is equivalent to an ensemble average over external potentials ψ. In brief notation,

$$(10.9)\qquad Z_N[\phi|U] = \langle Z_N[0|U+\psi]\rangle_\psi$$

where

$$(10.10)\qquad \langle F(\psi)\rangle_\psi = \frac{\iint F(\psi)\exp(-\frac{\beta}{2}\langle\psi|K|\psi\rangle)D\psi}{\iint \exp(-\frac{\beta}{2}\langle\psi|K|\psi\rangle)D\psi}$$

and

$$(10.11)\qquad \langle\psi|K|\psi\rangle = \int dxdy\, K(xy)\,\psi(x)\psi(y)\ .$$

Equation (10.8) is for purely attractive ϕ. Purely repulsive ϕ (K negative definite) is treated by replacing ψ by $i\psi$.

The corresponding grand canonical form of (10.9) is, easily,

$$(10.12)\qquad \mathfrak{z}[\phi|U] = \langle\mathfrak{z}[0|U+\psi]\rangle_\psi\ .$$

Differentiating (10.12) once with respect to U:

$$(10.13)\qquad n_1[x,\phi|U]\mathfrak{z}[\phi|U] = \langle\mathfrak{z}[0|U+\psi]n_1[x,0|U+\psi]\rangle_\psi$$

$$(10.14)\qquad n_1[x,\phi|U] = \frac{\langle n_1[x,0|U+\psi]\mathfrak{z}[0|U+\psi]\rangle_\psi}{\langle\mathfrak{z}[0|U+\psi]\rangle_\psi}\ ,$$

Expanding the notation in (10.12),

$$(10.15)\qquad \mathfrak{z}[\phi|U] = \frac{\iint \mathfrak{z}[0|U+\psi]\exp(-\frac{\beta}{2}\langle\psi|K|\psi\rangle)D\psi}{\iint \exp(-\frac{\beta}{2}\langle\psi|K|\psi\rangle)D\psi}\ ,$$

let us find the $\bar{\psi}$ which maximizes the integrand of the numerator.

The $\bar{\psi}$ must satisfy

$$\frac{\delta}{\delta\bar{\psi}}\left[\mathfrak{z}[0|U+\bar{\psi}]\exp -\frac{\beta}{2}\langle\bar{\psi}|K|\bar{\psi}\rangle\right] = 0 \tag{10.16}$$

or, using (10.11),

$$n_1[x,0|U+\bar{\psi}] + \int dy\, K(xy)\bar{\psi}(y) = 0\ , \tag{10.17}$$

$$\bar{\psi}(x) = \int dy\, n_1[y,0|U+\bar{\psi}]\phi(xy)\ . \tag{10.18}$$

If we approximate $n_1[x,0|U+\psi]$ by $n_1[x,0|U+\bar{\psi}]$ in (10.14), making it read

$$n_1[x,\phi|U] \cong n_1[x,0|U+\bar{\psi}], \tag{10.19}$$

the one particle distribution uncouples and

$$n_1[x,0|U+\bar{\psi}] = n\exp(-\beta U(x) - \beta\bar{\psi}(x))\ . \tag{10.20}$$

But $\bar{\psi}$ has been determined self-consistently, so that by (10.18),

$$\begin{aligned}\log n_1[x,0|U+\bar{\psi}] &= \log n - \beta U(x) \\ &\quad - \beta\int dy\, n_1[y,0|U+\bar{\psi}]\phi(xy)\ .\end{aligned} \tag{10.21}$$

If the external potential arises from a particle fixed at z,

$$U_\phi(x) = \phi(x,z) \tag{10.22}$$

$$(10.23) \qquad n_1[x,0|U_\phi + \overline{\Psi}] \equiv \frac{n_2(xz)}{n} \quad ,$$

equation (10.21) becomes

$$(10.24) \quad \log\left[\frac{n_2(xz)}{n^2}\right] = -\beta\phi(xz) - \frac{\beta}{n}\int dy\; n_2(yz)\phi(xy)$$

This is the non-linear Debye-Huckel equation (see ref. (1), p. 74).

11. Lattice Representation

Before the potential ensemble method can be successfully applied to quantum systems it is necessary to cast the partition function into an appropriate lattice form. We begin with the Boltzmann canonical partition function from (4.13):

$$(11.1) \quad Z_N = A^{MN}\int dx_1 \ldots dx_N \int dx_{1_{\beta_1}} \ldots dx_{N_{\beta_{M-1}}}$$

$$\exp -\sum_{k=1}^{M} \varepsilon\left[\sum_{i=1}^{N}\frac{m}{2\hbar^2}\dot{x}^2_{i_{\beta_k}} + \frac{1}{2}\sum_{i,j}^{N}{}' \,\phi(x_{i_{\beta_k}} - x_{j_{\beta_k}})\right]$$

$$\beta_M = \beta, \quad \beta_o = 0, \quad x_{1_o} = x_{1_\beta} \equiv x_1, \ldots,$$

$$x_{N_o} = x_{N_\beta} \equiv x_N \;.$$

The first transformation of (11.1) is to make the expression discrete in x space as well as in temperature.

Suppose that in each spatial dimension particles are restricted to a grid of discrete locations, spaced by Δ,

$$(11.2) \qquad \alpha_{i_{\beta_k}} = -\frac{L}{2}, -\frac{L}{2}+\Delta, \ldots, -\Delta, 0, \Delta, \ldots, \frac{L}{2}, \quad (\text{each } \beta_k),$$

there being Ω lattice sites in all along any line parallel to a coordinate axis, and

$$(11.3) \qquad \Omega\,\Delta = L .$$

Then

$$(11.4) \quad Z_N = \Delta^{MN} \sum_{\alpha_{1_{\beta_1}}} \cdots \sum_{\alpha_{N_{\beta_M}}} \exp - \sum_{k=1}^{M} \varepsilon \left[\frac{m}{2\hbar^2} \frac{\Delta^2}{\varepsilon^2} \sum_{i=1}^{N} (\alpha_{i_{\beta_k}} - \alpha_{i_{\beta_{k-1}}})^2 + \frac{1}{2} \sum_{i,j}^{N}{}' \phi(\alpha_{i_{\beta_k}} - \alpha_{j_{\beta_k}}) \right],$$

(see 4.11). When $\Delta \longrightarrow 0$ we recover (11.1). (Normalization factors will be omitted for simplicity in writing).

One other transformation will be made. Instead of the position representation (11.4), we will specify the number of particles at a particular lattice site. Also, the lattice sites will no longer exist in x-space alone, (11.2), (with the notation change $\alpha_{i_{\beta_k}} \longrightarrow x$), but in temperature dimension:

$$(11.5) \qquad \alpha = \beta', \beta' - \varepsilon, \beta' - 2\varepsilon, \ldots, 2\varepsilon, \varepsilon, 0,$$

M sites spaced by ε,

(11.6) $$M\varepsilon = \beta' , \qquad (\text{here } \beta' = (kT)^{-1}) ,$$

and particle number

(11.7) $$i = 1, 2, \ldots, N ,$$

spaced by unity. The quantity $\nu(xi\alpha)$ will mean the number of particles at the site (x,i,α).

In this "occupation representation"

(11.8) $$\sum_{k=1}^{M} \sum_{i=1}^{N} (\alpha_{i_{\beta_k}} - \alpha_{i_{\beta_{k-1}}})^2 = \sum_{xi\alpha} \sum_{yj\beta} \nu(xi\alpha)\nu(yj\beta)(x - y)^2 \delta_{ij}\, \delta_{|\alpha-\beta|,1} ,$$

since this interaction is iso-particle number and nearest neighbor in temperature.* Also

(11.9) $$\sum_{k=1}^{M} \frac{1}{2} \sum_{i} \sum_{\substack{j \\ i\neq j}} (\alpha_{i_{\beta_k}} - \alpha_{j_{\beta_k}}) = \frac{1}{2} \sum_{xi\alpha} \sum_{yj\beta} \nu(xi\alpha)\nu(yj\beta) \phi(x - y)\delta_{\alpha\beta} ,$$

an isothermal interaction.

Refer to the mixture analogy and diagram at the end of Section 4. We do not have to worry about inclusion of the self term on the right of (11.9), $(i = j)$, for reasons which appear shortly.

The partition function transcribes to

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* Note: x and α made dimensionless, by division by Δ, ε respectively.

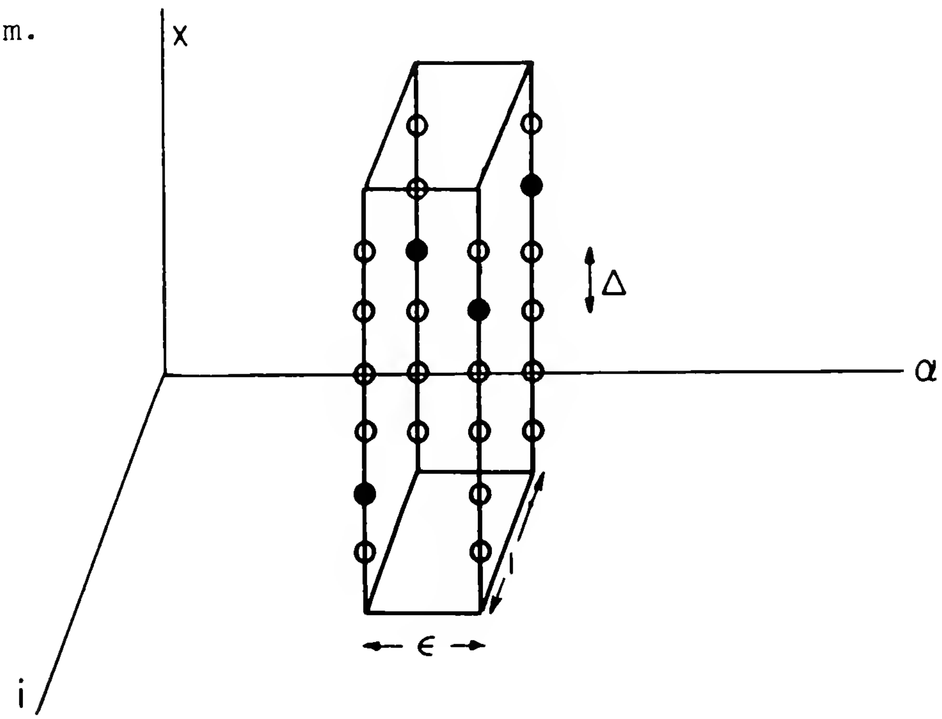
$$(11.10) \quad Z_N = \sum_{\{\nu(xi\alpha)\}}{}' \Delta^{NM} \exp - \varepsilon \sum_{xi\alpha} \sum_{yj\beta} \nu(xi\alpha)\nu(yj\beta)$$

$$\left[\frac{m\Delta^2}{2\hbar^2\varepsilon^2}(x - y)^2 \delta_{ij} \delta_{|\alpha-\beta|,1} + \frac{1}{2}\phi(x - y)\delta_{\alpha\beta}\right] .$$

All configurations of $\nu(xi\alpha)$ are summed subject to the following restriction: for every (i,α) pair we must have

$$(11.11) \qquad \sum_x \nu(xi\alpha) = 1 \text{ , (stronger than } \nu(xi\alpha) = 0, 1) \text{ ,}$$

for particle i at temperature α is to be found at one and only one point in space.[1] The five dimensional grid we are working with plus the exclusion (11.11) is shown in the diagram.



Every row of sites parallel to x axis has one and only one occupied site

[1] The total number of occupied sites is MN.

This restriction to the configurational sum may be dropped if we append an "exclusion potential" Φ with properties:

$$\Phi(xy\alpha\beta ij) = \infty \quad \text{when } i = j,\ \alpha = \beta \text{ simultaneously,} \tag{11.12}$$
$$= 0 \quad \text{elsewhere.}$$

We shall understand such a potential to be present in (11.10).

The appropriate boundary conditions on (11.10) for classical statistics are, for each i, to fold the (x,α) plane of sites into a cylinder joined at temperatures $(0,\beta')$ so that the vertical lines $\alpha = 0$, $\alpha = \beta'$ share the same sites. One of the virtues of the method to be developed is that boundary conditions need never be taken into account.

We next generate distributions in the usual way: append an external potential and differentiate.

Taking

$$U = \sum_{xi\alpha} \nu(xi\alpha)U(xi\alpha) \ , \tag{11.13}$$

$$\frac{\delta \log Z_N[U]}{-\delta U(x'i'\alpha')} = n_1(x'i'\alpha'|U) \ , \tag{11.14}$$

$$\frac{\delta n_1(x'i'\alpha'|U)}{-\delta U(\bar{x}\ \bar{i}\ \bar{\alpha})} = n_2(x'i'\alpha',\bar{x}\bar{i}\bar{\alpha}|U) + n_1(x'i'\alpha'|U)\delta_{x'i'\alpha',\bar{x}\bar{i}\bar{\alpha}}\ \Delta^{-1} - n_1(x'i'\alpha'|U)n_1(\bar{x}\bar{i}\bar{\alpha}|U) \ , \tag{11.15}$$

where

$$(11.16) \quad n_1(x'i'\alpha') = Z_N^{-1} \sum_{\{\nu(\overline{xi\alpha})\}} \Delta^{NM-1} \nu(x'i'\alpha') \exp - [\ ]\ ,$$

and

$$(11.17) \quad n_2(x'i'\alpha', \overline{xi\alpha}) = Z_N^{-1} \sum_{\{\nu(\overline{xi\alpha})\}} \Delta^{NM-2} \nu(x'i'\alpha')\nu(\overline{xi\alpha}) \exp - [\ ]\ .$$

These functions are related to the space-temperature distributions of the path integral methods: taking $\lim_{\Delta \to 0}$,

$$(11.18) \qquad \sum_{i=1}^{N} n_1(xi\alpha) = n_1(x\alpha)\ ,$$

$$(11.19) \quad \sum_{i=1}^{N} \left[n_2(xi\alpha, yi\beta) + n_1(xi\alpha)\delta_{x\alpha,y\beta} \cdot \Delta^{-1} \right] = n_2(x\alpha y\beta)\ , \quad \text{" self "},$$

$$(11.20) \qquad \sum_{\substack{i=1 \\ i \neq j}}^{N} \sum_{j=1}^{N} n_2(xi\alpha, yj\beta) = n_2(x\alpha; y\beta)\ , \quad \text{" mutual "}\ .$$

The second term in (11.19) picks up the singularity in the self distribution when $\alpha = \beta$, (see discussion after (3.13)).

Bootstrap Operation

The density in an external potential due to a single occupied lattice site is proportional to the pair distribution for a uniform system. To see this isolate an occupied site at $\overline{xi\alpha}$, $\nu(\overline{xi\alpha}) = 1$. This site supplies an external potential to the others:

(11.21) $$U_{\phi+KE} = \sum_{xi\alpha} \nu(xi\alpha)\nu(\bar{x}\bar{i}\bar{\alpha}) \left[\frac{m\Delta^2}{\hbar^2\varepsilon^2}(x-\bar{x})^2 \delta_{i,\bar{i}}\,\delta_{|\alpha-\bar{\alpha}|,1} + \phi(x-\bar{x})\delta_{\alpha,\bar{\alpha}}\right].$$

The density in the presence of $U_{\phi+KE}$ is:

(11.22) $$n_1(x'i'\alpha'|U_{\phi+KE}) = \frac{\sum'_{\{\nu(xi\alpha)\}} \Delta^{NM-1}\, \nu(x'i'\alpha')\exp - [\ ]'\exp -\varepsilon U_{\phi+KE}}{\sum'_{\{\nu(xi\alpha)\}} \Delta^{NM} \exp - [\ ]' \exp -\varepsilon U_{\phi+KE}}$$

the prime on the exponential meaning that the site $\nu(\bar{x}\bar{i}\bar{\alpha})$ is excluded from the sums appearing there. This site enters into $U_{\phi+KE}$ only. Similarly, the prime on the configuration sum means the sum is taken over a lattice in which the one site at $(\bar{x}\bar{i}\bar{\alpha})$ has been excluded. Dividing top and bottom by Δ in (11.22), we see that this is precisely the meaning of $\frac{n_2(x'i'\alpha',\bar{x}\bar{i}\bar{\alpha})}{n_1(\bar{x}\bar{i}\bar{\alpha})}$ defined on the full lattice - i.e. augmented now by $(\bar{x}\bar{i}\bar{\alpha})$. So

(11.23) $$n_1(x'i'\alpha' \mid U_{\phi+KE}) = \frac{n_2(x'i'\alpha',\bar{x}\bar{i}\bar{\alpha})}{n_1(\bar{x}\bar{i}\bar{\alpha})} .$$

This relation has the simplicity of the classical one, see (2.16). It is just at this point that the relation to the path integral methods becomes apparent: had we fixed an array of occupied sites one per α value, $\alpha = 0,\ldots, M$, (i = constant), the resulting bootstrap equations would be the same as in Section 5.

The next step has been to expand directly $n_1[U]$ v. U in a Taylor series. Here we are in a dilemma. If we expand in the full $U_{\phi+KE}$, the KE is so strong $(\sim\varepsilon^{-1}(x-y)^2)$ it overpowers the pair interaction resulting in nonsense, while if we expand in U_ϕ, it is too weak, $(\sim\varepsilon)$, to give any correction to free particle solutions. The potential ensemble removes these difficulties by replacing the pair potential by an external potential $\bar{\psi}$ determined self-consistently.

12. Application of Potential Ensemble to the Lattice Representation

Working with a more general pair potential $\phi(xi\alpha,yj\beta)$, and with kinetic energy and exclusion potential,

$$\theta(xi\alpha,yj\beta) = \frac{m\Delta^2}{\hbar^2\varepsilon^2}(x-y)^2\,\delta_{ij}\,\delta_{|\alpha-\beta|,1} + \Phi(xi\alpha,yj\beta) \quad , \tag{12.1}$$

(11.10) becomes, in brief notation:

$$(12.2)\quad Z_N[\theta+\phi|U]$$

$$= \sum_{\{\nu(x)\}} \Delta^{NM} \exp\left[-\varepsilon\sum_{x,y}\nu(x)\nu(y)\left[\tfrac{1}{2}\,\theta(xy) + \tfrac{1}{2}\,\phi(xy)\right]\right]$$

$$\cdot \exp - \varepsilon\sum_{x}\nu(x)U(x) \ .$$

We have added an external potential, and used the notation $x \equiv (xi\alpha)$, $y \equiv (yj\beta)$.

Allocate the ϕ to an external potential ψ using occupied lattice sites as sources:

$$\psi(x) = \sum_y \phi(xy)\nu(y) \quad . \tag{12.3}$$

If $K(xy)$ is the matrix inverse of $\phi(xy)$:

$$\sum_y K(xy)\phi(yz) = -\delta_{xz} \quad , \tag{12.4}$$

so that

$$\sum_y K(xy)\psi(y) + \nu(x) = 0 \quad , \tag{12.5}$$

the potential energy assumes the form

$$\frac{1}{2}\sum_{x,y} \nu(x)\nu(y)\phi(xy) = \sum_x \nu(x)\psi(x) + \frac{1}{2}\sum_{x,y} K(xy)\,\psi(x)\psi(y) \quad . \tag{12.6}$$

In analogy to (10.8),

$$Z_N[\theta + \phi|U] = \sum_{\{\nu(x)\}} \Delta^{NM} \frac{\displaystyle\iint \exp - \varepsilon \sum_{x,y} \nu(x)\nu(y)\frac{\theta(xy)}{2} \cdot \exp - \varepsilon \sum_x \nu(x)(\psi(x) + U(x)) \cdot \exp -(\frac{\varepsilon}{2}\sum_{x,y} K(xy)\psi(x)\psi(y))D\psi(x)}{\displaystyle\iint \exp(-\frac{\varepsilon}{2}\sum_{x,y} K(xy)\psi(x)\psi(y))D\psi(x)} \quad , \tag{12.7}$$

briefly,

$$(12.8) \qquad Z_N[\theta + \phi|U] = < Z_N[\theta|U + \psi] >_\psi$$

A differentiation with respect to U yields:

$$(12.9) \quad n_1(x,\theta + \phi|U) = \frac{< n_1(x,\theta|U + \psi)Z_N[\theta|U + \psi] >_\psi}{< Z_N[\theta|U + \psi] >_\psi}$$

The $\overline{\psi}$ which maximizes the numerator of (12.8) is given by

$$(12.10) \qquad \overline{\psi}(x) = \sum_y \Delta\phi(xy)n_1(y,\theta|U + \overline{\psi}) ,$$

compare (10.18).

Now let us approximate $n_1(x,\theta|U + \psi)$ by $n_1(x,\theta|U + \overline{\psi})$ in (12.9) making it read

$$(12.11) \qquad n_1(x,\theta + \phi|U) = n_1(x,\theta|U + \overline{\psi}) .$$

Suppose now that U arises from an occupied lattice site at z, so that it is composed of two parts, kinetic and potential energies:

$$(12.12) \qquad U = U_\theta + U_\phi .$$

Expand $n_1(x,\theta|U_\theta + U_\phi + \overline{\psi})$ v. $U_\phi + \overline{\psi}$, using (11.15),

$$(12.13) \quad n_1(x,\theta|U_\theta + U_\phi + \overline{\psi}) = n_1(x,\theta|U_\theta) - \sum_y [n_2(x\,y,\theta|U_\theta) + n(x,\theta|U_\theta)\frac{\delta_{xy}}{\Delta} - n(x,\theta|U_\theta)n(y,\theta|U_\theta)]\varepsilon\Delta\,(U_\phi + \overline{\psi})(y) + \dots \; .$$

But $\overline{\psi}(y)$ has been determined self-consistently by (12.10), so substituting this into (12.13),

$$(12.14) \quad n_1(x,\theta|U_\theta + U_\phi + \overline{\psi}) = n_1(x,\theta|U_\theta) - \sum_y [n_2(x\,y,\theta|U_\theta) + n(x,\theta|U_\theta)\frac{\delta_{x\,y}}{\Delta} - n(x,\theta|U_\theta)n(y,\theta|U_\theta)]\varepsilon\Delta \cdot [U_\phi(y) + \sum_\omega \Delta\phi(y\omega)n_1(\omega,\theta|U_\theta + U_\phi + \overline{\psi})] \; .$$

Now $U_\phi + \overline{\psi}$ is tied to the fixed occupied site at z,

$$(12.15) \qquad U_\phi(y) = \phi(yz) \; ,$$

and

$$(12.16) \qquad n_1(x,\theta|U_\theta + U_\phi + \overline{\psi}) \equiv \frac{n_2(xz)}{n_1(z)}$$

using (11.23) and (12.11).

Equation (11.23) also means that

$$(12.17) \qquad n_1(x,\theta|U_\theta) = \frac{n_2^o(xz)}{n_1^o(z)} ,$$

and by a simple generalization of (11.23),

$$(12.18) \qquad n_2(xy,\ \theta|U_\theta) = \frac{n_3^o(xyz)}{n_1^o(z)} .$$

Substituting all of these into (12.14),

$$(12.19) \quad n_2(xz) = n_2^o(xz) - \sum_{y,\omega} [n_3^o(xyz) + n_2^o(xz) \frac{\delta_{xy}}{\Delta} - n_2^o(xz) \frac{n_2^o(yz)}{n_1(z)}] \frac{1}{n_1(z)} \cdot \varepsilon\Delta^2 \phi(y\omega)[n_2(\omega z) + n_1(z) \frac{\delta_{\omega z}}{\Delta}] ,$$

an integral equation for $n_2(xz)$. One equation suffices, for if $n_2(xz)$ is found, the self and mutual pair distributions with space and temperature arguments only are gotten via (11.17) - (11.19).

If we perform a superposition approximation in the first bracket of (12.19), separating out the z dependence:

$$(12.20) \quad n_2(xz) = n_2^o(xz) - \sum_{y,\omega} [n_2^o(xy) + n_1(x) \frac{\delta_{xy}}{\Delta} - n_1(x)n_1(y)]\varepsilon\Delta^2 \cdot\phi(y\omega)[n_2(\omega z) + n_1(z) \frac{\delta_{\omega z}}{\Delta}] .$$

The potential is isothermal and has no dependence on particle number. So that expanding the notation:

$$(12.21)\quad n_2(xi\alpha, zk\nu) = n_2^o - \sum_{y,\omega} \sum_{\beta} [n_2^o(xi\alpha, yj\beta) + n(xi\alpha)\delta_{xi\alpha,yj\beta}\,\Delta^{-1} - n(xi\alpha)n(yj\beta)] \cdot \varepsilon\Delta^2\,\phi(y-\omega)[n_2(\omega\ell\beta, zk\nu) + n(zk\nu)\Delta^{-1} \cdot \delta_{\omega\ell\beta,zk\nu}] .$$

The easiest way to compare this to earlier work is to sum i, j, k and ℓ independently from 1 to N. Then according to (11.17) - (11.19), ε, $\Delta \longrightarrow 0$,

$$(12.22)\quad n_2(x\alpha;z\nu) + n_2(x\alpha z\nu) = n_2^o(;) + n_2^o(\ ) - \int_0^{\beta'} dy\,d\omega\,d\beta[n_2^o(x\alpha;y\beta) - n^2 + n_2^o(\ )]\phi(y-\omega) \cdot [n_2(\omega\beta;z\nu) + n_2(\ )] .$$

Replacing $n_2(\ )$ by $n_2^o(\ )$, leaves us with (7.8) in classical statistics or (9.6) in quantum statistics (with $\tilde{n}$ replaced by $\tilde{n}^o$ in (9.6)).

The method developed here puts both statistics on an equal footing because the boundary conditions on Z_N and the distributions never enter.

It is not really necessary to make the separate approximation $n_2(\ ) = n_2^o(\ )$. If (12.22) is solved this approximation will result when the thermodynamic limit ($N \longrightarrow \infty$, $V \longrightarrow \infty$, $\frac{N}{V} = n$) is taken.

Equation (12.19) is an improved approximation over

(12.20). Also, we could carry out the Taylor expansion (12.13) to higher orders. In addition one can improve the steepest descent calculation represented by (12.11). To do this go back to (12.9) and expand $n_1(x,\theta|U+\psi)$ about $\overline{\psi}$:

$$(12.23)\quad n_1(x,\theta|U+\psi) = n_1(x,\theta|U+\overline{\psi}) - \sum_y [n_2(xy,\theta|U+\overline{\psi}) + n_1(x,\theta|U+\overline{\psi})\frac{\delta_{xy}}{\Delta} - n_1(x,\theta|U+\overline{\psi})n_1(y,\theta|U+\overline{\psi})] \cdot \Delta\varepsilon(\psi(y) - \overline{\psi}(y)) + \ldots \quad .$$

The n_2 in the bracket can be expressed in terms of $n_1(x,\theta|U+\overline{\psi})$ by a Taylor expansion similar to (12.13) with the self-consistency relation (12.10) employed once more. Expectations over powers of ψ would have to be done (requiring a specific ϕ and boundary conditions) to improve upon (12.11).

Appendix

Notation For Path Integral Methods

n_s, distributions

$\hat{n}_s$, modified distributions

F_s, Ursell Functions

$\hat{F}_s$, modified Ursell Functions

$n_2(\ )$, n_2, self pair distribution

$n_2(;)$, mutual pair distribution

$\overline{n} = n_2(;) - n^2$

n_1, n, density

$\tilde{n}$, see (8.26)

^{o} = "free"

$n_2(k, \alpha)$, Fourier transform, self pair distribution

<u>Bibliography</u>

[1] J. K. Percus, Pair Distribution Function in Classical Statistical Mechanics, in Equilibrium Theory of Classical Fluids, H. L. Frisch, J. L. Lebowitz (W. A. Benjamin, 1964).

[2] L. Landau and I. Lifshitz, Statistical Physics, (Addison-Wesley, Reading 1958), 231.

[3] J. K. Percus and G. J. Yevick, Phys. Rev. <u>110</u>, 1 (1958).

[4] J. G. Kirkwood and Z. Salsburg, Discussions Faraday Soc. <u>15</u>, 28 (1953).

[5] J. E. Mayer and E. Montroll, J. Chem. Phys. <u>9</u>, 2 (1941).

[6] J. L. Lebowitz and J. K. Percus, J. Math. Phys. <u>4</u>, 1495 (1963).

[7] J. K. Percus, Transactions of N. Y. Academy of Sciences, Sec. II, Vol. 26, Suppl. to no. 8, 1062 (1964).

[8] R. P. Feynman and A. R. Hibbs, Quantum Mechanics and Path Integrals, (McGraw-Hill, 1965).

[9] J. K. Percus, Many Body Systems, CIMS Lecture Notes, Winter 1965.

[10] E. W. Montroll and J. C. Ward, Physics of Fluids <u>1</u>. 55 (1958).

[11] J. L. Lebowitz and J. K. Percus, J. Math. Phys. <u>4</u>, 116 (1963).

[12] E. W. Montroll, in Lectures in Statistical Mechanics (Appendix), G. E. Uhlenbeck, G. W. Ford (Amer. Math. Soc., 1963), 143.

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